

Electrical and optical properties of TiO_2 in accumulation and of lithium titanate $\text{Li}_{0.5}\text{TiO}_2$

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Changes in the optical absorption and electrical conductivity of dense and mesoporous anatase TiO_2 films were measured *in situ* as a function of electrode potential during electrochemical lithium intercalation. A special two-electrode geometry was used for the conductivity measurements, in which the contacts were separated by a small gap bridged by the TiO_2 . When electrons are injected, an accumulation layer is formed and the conductivity increases several orders of magnitude. A monotonic increase of the optical absorption with wavelength confirms the presence of (partially) delocalized electrons. Insertion of lithium ions results in the formation of the $\text{Li}_{0.5}\text{TiO}_2$ phase and a decrease of the overall conductance. The specific conductivity of the $\text{Li}_{0.5}\text{TiO}_2$ phase is (9.1 ± 0.2) S/cm, significantly lower than that of Li-doped anatase TiO_2 . This is corroborated by the absorption spectrum of $\text{Li}_{0.5}\text{TiO}_2$, which shows two pronounced peaks around 440 and 725 nm and no characteristic free-electron features. At potentials below 1.7 V vs Li additional lithium could be inserted into $\text{Li}_{0.5}\text{TiO}_2$, and the conductance was found to increase again. The results are discussed in terms of possible changes in the electronic structure that are induced by the insertion of lithium ions. © 2001 American Institute of Physics. [DOI: 10.1063/1.1388165]

I. INTRODUCTION

Anatase TiO_2 is well known for its ability to accommodate charge in the form of interstitial lithium ions. Intercalation proceeds by a first-order phase transition



The existence of the orthorhombic $\text{Li}_{0.5}\text{TiO}_2$ phase is well documented.¹ Evidence also exists for a solid solution phase Li_xTiO_2 ($x \leq 0.05$),² and lithium titanates with Li/Ti ratio larger than 0.5.^{3,4} The low cost, ease of preparation, and the relatively fast kinetics make TiO_2 an attractive material for lithium ion batteries^{5,6} and electrochromic devices. The latter is based on the coloration from transparent to dark blue and, finally, black during intercalation.^{7,8}

The origin of the coloration is much debated. Some have attributed it to absorption by free electrons that are present to charge compensate either intercalated lithium ions, or cations accumulated at the solid/liquid interface.^{9–11} The latter is of particular importance in the case of high surface area mesoporous TiO_2 . Others have attributed the color to polaron absorption by electrons localized at Ti^{III} ions in the lattice,^{12,13} and to electrons trapped in surface states.¹⁴

Surprisingly little is known about the electronic conductivity of Li_xTiO_2 , despite its implications for the validity of the models used to describe the optical properties, and its important role in electron and ion transport. A low conductivity causes ohmic losses inside the electrode, which has a detrimental influence on the device efficiency. A high conductivity reduces the electric field, which can slow down ion

transport. Clearly, detailed knowledge of the electrical properties as a function of lithium content is required to further optimize the device performance.

The aim of this work is to investigate the correlated changes in the electrical conductivity and optical absorption that occur upon electron injection and lithium intercalation in anatase TiO_2 . Special attention will be devoted to the properties of $\text{Li}_{0.5}\text{TiO}_2$. Both mesoporous and smooth dense films are studied to discriminate between surface and bulk effects, and to determine the role of interparticle electron transport. The simple topology of dense films facilitates quantitative analysis of the data, while the nanostructured morphology is preferred in practical devices.

Investigations of Li_xTiO_2 are severely hampered by its instability in air. Exposure to moisture, and to a lesser extent oxygen, causes rapid reaction at the surface to form Li_2O and LiOH . Lithiated TiO_2 nanoparticles can change from black to white in a few seconds when exposed to air. Hence, reliable analysis necessitates strictly controlled environmental conditions during preparation and characterization, or *in situ* characterization techniques.

The effects of both electron injection and lithium intercalation can be conveniently studied *in situ* by placing the sample in an electrochemical cell. This allows for direct control of the electrochemical potential, i.e., the Fermi level, of the system and the amount of accumulated charge. Potential control is especially important when cation accumulation at the solid/liquid interface occurs, since the charge distribution at the interface changes instantly when the material is taken out of the electrolyte solution. Electrochemical lithiation also allows for easy integration of charge to determine the amount of electrons accumulated, and for straightforward

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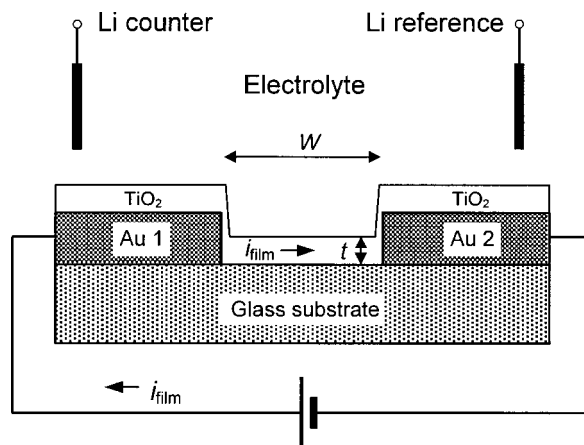


FIG. 1. Schematic drawing of the electrode geometry. The two gold working electrodes (Au 1 and 2) are separated by a small gap ($W=10$ or $20\ \mu\text{m}$) that is filled with either a mesoporous or a dense TiO_2 film with a thickness t . It should be noted that the drawing is not to scale, t being at least ten times smaller than W .

discrimination between reversible and irreversible changes upon repeated (de-)lithiation.

While *in situ* optical measurements are trivial, a special sample configuration is necessary to measure the conductivity in contact with an electrolyte. The method was originally developed by Wrighton and co-workers,¹⁵ and has been used recently to measure the electron mobility in nanoparticulate ZnO electrodes.¹⁶ It is based on a geometry with two independent working electrodes and is shown schematically in Fig. 1. Two inert electrodes are separated by a small gap, which is filled by the material to be studied. The electrodes are functionally equivalent, and are analogous to the drain and source of a field effect transistor. The electrochemical potentials of both electrodes can be individually controlled by connecting them to the working electrode inputs of a bipotentiostat. The resistance of the TiO_2 can be measured by applying a small potential difference between the electrodes, and measuring the current between them (i_{film} in Fig. 1).

II. EXPERIMENT

Nanostructured, porous anatase TiO_2 samples were prepared from a colloidal solution of nanosized TiO_2 (Solaronix SA, average particle diameter about 15 nm). The solution was diluted with 50% (by mass) of ethanol in order to prevent film cracking during evaporation of the solvent. The resulting paste was equally distributed over gold- or indium tin oxide (ITO)-coated glass substrates by doctor blading, using a single layer of Scotch tape (3M) to determine the green film thickness. The area of the substrates was approximately $20 \times 15\ \text{mm}^2$. For the resistance measurements, a 10 or $20\ \mu\text{m}$ gap separated the two gold contacts. After drying for 30 min at room temperature, a heat treatment was applied for 30 min at $150\ ^\circ\text{C}$ in air. Thicker layers were made by repeated film application and annealing, with each layer having a thickness of about $1\ \mu\text{m}$. As a final step, the films were annealed for 2 h at $450\ ^\circ\text{C}$ in air to sinter the particles. The substrates were weighed before deposition and after the final

anneal step to yield the amount of TiO_2 deposited. The resulting films had about 50% porosity, were optically transparent, and showed no signs of cracks. Interference patterns indicated that the thickness homogeneity is excellent, except at the very edge of the samples.

Dense anatase TiO_2 films were deposited on similar substrates by electron beam evaporation (Biorad VC6800 vacuum evaporator) of reduced TiO_2 powder (rutile, 99.95%, Acros Chimica). During deposition the oxygen partial pressure was 2×10^{-3} mbar. The base pressure of the system was less than 2×10^{-6} mbar. The substrate temperature was $150\ ^\circ\text{C}$, and the growth rate of the films was $2\ \text{nm/min}$. Further details are described elsewhere.¹⁷ The thickness of the films could be monitored during growth by a quartz crystal microbalance. Films with a random crystallite orientation were grown, with a thickness of 26, 50, and $150\ \text{nm}$.

The profile of the amount of TiO_2 across the gap in the resistance measurements was determined with electron probe microanalysis (Cameca SX50 Microprobe). The amount of TiO_2 per unit area deposited in the gap was found to be equal to the amount deposited on the gold contacts for both nanostructured and dense films.

Electrochemical experiments were performed in a three-electrode electrochemical cell. Lithium foil was used as a counter and as a reference electrode. The entire sample was immersed in an electrolyte solution of 1.0 M LiClO_4 in propylene carbonate. Potential control was provided by an Autolab PG20 potentiostat or an EG&G Model 366A bipotentiostat. Resistance measurements were performed with the bipotentiostat (in the double layer regime, see below) or with a Keithley 2420 sourcemeter (in the intercalation regime), and were corrected for the contact resistances and for the gold or ITO sheet resistance. All resistance measurements were carried out in an argon-filled glovebox ($<1\ \text{ppm}\ \text{H}_2\text{O}$, O_2). The voltage difference between the working electrodes was typically $\leq 10\ \text{mV}$ at relatively positive potential, and $\leq 2\ \text{mV}$ at relatively negative potential. The current through the gap was invariably proportional to the voltage difference applied. The optical absorption of the films was measured with a Perkin-Elmer Lambda 19 spectrophotometer using an air-tight cell which was assembled in the glovebox.

III. RESULTS

A. Charge injection

Figure 2 shows a cyclic voltammogram of a 26 nm evaporated TiO_2 film at a scan rate of $25\ \mu\text{V/s}$. Three regimes can be distinguished. In the “double layer regime” between 2.5 V and 1.8 V, electrons are injected into the space charge region inside TiO_2 . Charge compensation occurs at the electrode | electrolyte interface by adsorption and/or redistribution of charged electrolyte species. Accordingly, the charge injected is independent of thickness for dense films, and proportional with thickness for mesoporous films. The total charge consumed in this regime is relatively small, in the order of $0.5\ \text{mC/cm}^2$.

At a potential of $\approx 1.80\ \text{V}$, close to the onset of the phase transition described by Eq. (1), the charge compensation mechanism changes. Electron injection is now accompanied

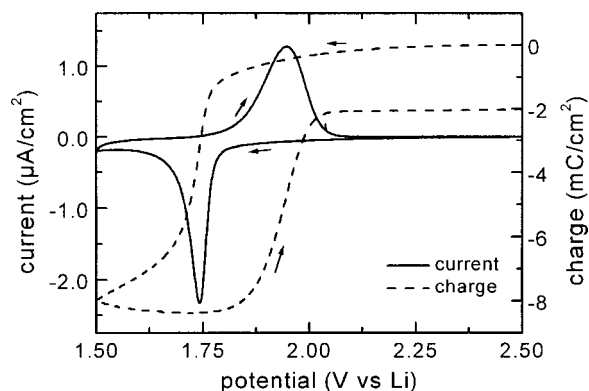


FIG. 2. Cyclic voltammogram of a 26 nm TiO_2 film deposited on a gold-coated glass substrate. The scan rate was $25 \mu\text{V/s}$. The total extracted charge is 6.3 mC/cm^2 , which corresponds to an overall composition of $\text{Li}_{0.5}\text{TiO}_2$.

by intercalation of lithium ions which provide local charge compensation. First, a $\text{TiO}_2\text{:Li}$ solid solution may be formed. At insertion ratios beyond the solubility limit, which is estimated to be $\leq 5 \text{ at. \%}$,^{2,18} the Li-doped TiO_2 undergoes the phase transformation to $\text{Li}_{0.5}\text{TiO}_2$.^{1,17,18} This corresponds to the cathodic current peak in Fig. 2. The phase transformation can be reversed by going to positive potentials,¹⁸ as indicated by the anodic current peak. The amount of charge associated with both current peaks is identical (6.3 mC/cm^2) and corresponds to an overall composition of $\text{Li}_{0.5}\text{TiO}_2$. This shows that the film can be fully transformed into the lithium titanate phase. In contrast, similar measurements on a 150 nm dense film show that the degree of intercalation is limited. 38% of the theoretical charge can be inserted, which implies that only the outer 57 nm of the films is transformed.¹⁹ This limit points to a negligible rate of additional Li uptake and is most likely a manifestation of compressive strain,¹⁷ caused by the 4% larger unit cell volume of $\text{Li}_{0.5}\text{TiO}_2$ compared to that of anatase TiO_2 .

The current–voltage curves for mesoporous TiO_2 films, reported elsewhere,¹⁸ are similar to those in Fig. 2. The cathodic and anodic current peaks are located at the same potentials. One small difference concerns the intercalation capacity, which is often somewhat smaller ($\approx 90\%$) than the theoretical capacity. Some parts of the film, especially at the thicker edges of the samples, may be in poor electrical contact, which prevents the insertion of lithium ions. The presence of a small fraction of rutile TiO_2 , which shows (almost) no intercalation,²⁰ is another possibility. Strain effects are believed to be less important here, since the open structure of the porous film can more easily accommodate the induced strain.

The third regime starts when all anatase TiO_2 has been converted to $\text{Li}_{0.5}\text{TiO}_2$, i.e., below about 1.7 V. Additional lithium may be inserted into $\text{Li}_{0.5}\text{TiO}_2$ if the driving force for lithium insertion is sufficiently high. The current in this “ $\text{Li}_{0.5}\text{TiO}_2$ regime” is dominated by (irreversible) side reactions, such as reductive electrolyte decomposition. The extent to which side reactions occur depends on the potential window and the scan rate. Overall charge reversibilities range from 75% in Fig. 2 to over 95% for mesoporous

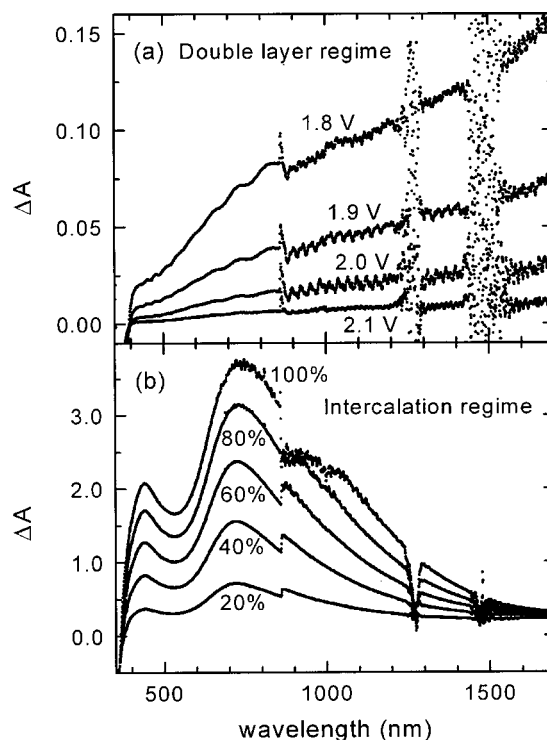


FIG. 3. Optical absorption difference (ΔA) spectra of a $1.1 \mu\text{m}$ mesoporous TiO_2 film on ITO-coated glass in (a) the double layer regime and (b) the intercalation regime. The reference spectrum is recorded at 2.5 V vs Li. The spectrum in the double layer regime indicates free-electron absorption, while the absorption peaks in the intercalation regime indicate the presence of bound electrons in the $\text{Li}_{0.5}\text{TiO}_2$ phase. The large scatter observed around 1280 and 1500 nm is due to electrolyte absorption. The irregularities at 860 nm are due to a filter change in the spectrometer.

samples at scan rates higher than 1 mV/s . More detailed investigations of electrochemical side reactions occurring in the TiO_2 /propylene carbonate system can be found elsewhere.^{21,22}

For the measurements reported below in Sec. III B charge refers to *reversible* charge only, as determined by the reoxidation, i.e., anodic current during a reverse scan in the direction of 2.5 V or higher. We made sure the system was in equilibrium in two ways. Optical and conductivity measurements did not vary with time at a given potential, and the anodic reversible charge was independent of waiting time at the measurement potential. Hence, the possibility of side reactions influencing the optical absorption or electrical conductivity can be excluded. Equilibration typically took less than one minute in the double layer regime, and several tens of minutes in the intercalation regime.

B. Optical absorption

Figure 3(a) shows the difference absorption spectra (ΔA) of a $1.1 \mu\text{m}$ mesoporous film in the double layer regime. A monotonous increase with wavelength is observed, which is strongly reminiscent of absorption by delocalized electrons.²³ This is corroborated by a pronounced absorption decrease around 350 nm (not shown), close to the band gap. This so-called *Moss–Burstein* shift is caused by (nearly-)free electrons occupying the bottom of the conduction band, and is a well-known phenomenon for TiO_2 in accumulation.⁹ In

TABLE I. Coloration efficiencies of mesoporous and dense TiO_2 films at various wavelengths in the double layer (CE_{dbl}) and intercalation (CE_{int}) regimes. The absorption of dense films in the double layer regime is too small to be measured.

Morphology	CE	Peak@440 nm	Peak@725 nm	1300 nm	1700 nm
Mesoporous	$\text{CE}_{\text{dbl}} (\text{cm}^2/\text{C})$	3.6	12.5	18	25
	CE_{int}	21	37	8	<1
Dense		Peak@390 nm ≈ 18	Peak@700 nm 34	1300 nm 11.5	1700 nm ≈ 3
	CE_{int}				

the remainder of this article, we will refer to these electrons as (nearly) free, as we cannot differentiate between electrons in shallow trap states and completely delocalized electrons. As more electrons are injected the free-electron absorption increases. The overall absorption in the double layer regime is quite small, and the TiO_2 film remains transparent to the naked eye down to 1.8 V. For dense films the change in absorption was too small to be measured accurately.

Following complete intercalation at 1.7 V, lithium was extracted galvanostatically in steps of 20%. After each step, the absorption spectrum was recorded under open circuit conditions. The results for mesoporous films are shown in Fig. 3(b). Clearly, intercalation results in a significant increase of the absorption and a marked change of the shape of the spectrum. Two broad peaks are observed around 440 and 725 nm. This implies that electrons in $\text{Li}_{0.5}\text{TiO}_2$ are less free than in TiO_2 in the double-layer region, and that the dark color of $\text{Li}_{0.5}\text{TiO}_2$ cannot be attributed to (nearly-)free electrons but rather to localized electrons. The low absorption at 1700 nm is in agreement with this. The main features of the absorption difference spectra for dense films are identical to those in Fig. 3(b). A closer look reveals some small differences between dense and porous films, which are discussed later.

The absorption is further analyzed as a function of injected charge Q at the absorption maxima (440 and 725 nm, and 390 and 700 nm for the porous and dense films, respectively), and at 1300 and 1700 nm. A linear relationship is found between ΔA and Q in both regimes, independent of layer thickness. The coloration efficiency CE (cm^2/C) is calculated from the slope. The results are summarized in Table I. The CE values for both types of film are very similar in the intercalation regime, and in good agreement with earlier reports.^{8,24–26}

For the dense films, the first peak is found at a 50 nm smaller wavelength. Although this may be partly caused by a true difference in the physical properties of the absorption centers, two other effects play a role. First, the absorption spectra of the dense films show relatively strong interference fringes around 400 nm. The position of these fringes changes upon intercalation due to the change in refractive index,²⁷ and they do not completely cancel out anymore in the difference absorption spectra. Furthermore, an accumulation layer may be present even after the phase transformation, i.e., in the $\text{Li}_{0.5}\text{TiO}_2$ phase. This is consistent with the presence of the absorption shift around 350 nm for fully intercalated $\text{Li}_{0.5}\text{TiO}_2$ films (not shown). Since the accumulation layer in a dense film occupies a smaller volume fraction than in a

nanoparticulate film, the induced Moss–Burstein shift is also smaller. This may cause an additional error in the determination of the peak position and CE.

The position of the long-wavelength peak and the CE values at 700/725, 1300 and 1700 nm also differ slightly for the two film morphologies. This indicates subtle differences in the materials properties such as the crystallinity²⁸ and, in the case of thin dense films, the presence of uniaxial stress.²⁹ In the literature a broad range of peak positions and CE values is found, which encompasses the values found here.

C. Electrical conductivity

An important requirement is that all current flows through the film; additional current pathways (from “source” to “drain”) through the electrolyte should be avoided. This requirement is fulfilled if the measured resistance is proportional to the gap width and inversely proportional to the film thickness.¹⁶ This is always observed for porous as well as dense films in both the accumulation and intercalation regimes, which proves that the measured resistance is, indeed, that of the material in the gap between the two working electrodes.

Some results for a mesoporous film are shown in Fig. 4. The conductance displays a characteristic “sawtooth” pattern. A steep increase is observed in the double layer regime, consistent with the formation of an accumulation layer and the free-electron absorption observed in Fig. 3(a). The con-

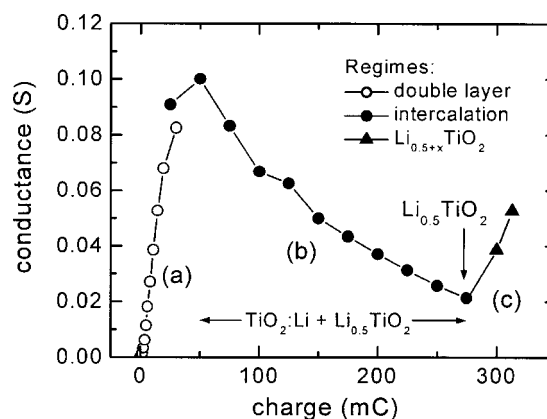


FIG. 4. Conductance vs charge for a mesoporous TiO_2 electrode with a 10 μm gap and a thickness of $\sim 1 \mu\text{m}$. Three regimes can be distinguished: (a) the double layer regime comprising undoped TiO_2 with a space charge region present; (b) the intercalation regime, where $\text{Li}_{0.5}\text{TiO}_2$ coexists with Li-doped TiO_2 ; (c) beyond the intercalation regime, where $\text{Li}_{0.5+x}\text{TiO}_2$ is present.

TABLE II. Conductivity and mobility values for nanostructured and dense films measured in different regimes. Values in the double layer regime ($\text{TiO}_2 + e^-$) are measured at +2.0 V vs Li.

Morphology	Regime	σ (S/cm)	μ ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)
Mesoporous	$\text{TiO}_2 + e^-$	1.8	0.05
	$\text{Li}:\text{TiO}_2^a$	0.75	0.005
	$\text{Li}_{0.5}\text{TiO}_2$	0.42 ± 0.04	$(2.5 \pm 0.1) 10^{-4b}$
	$\text{Li}_{0.5+x}\text{TiO}_2^c$	1.7 ± 0.6	...
Dense	$\text{TiO}_2 + e^-$	200 ± 50	1.5 ± 0.3
	$\text{Li}:\text{TiO}_2$	57 ± 7	0.2^d
	$\text{Li}_{0.5}\text{TiO}_2$	9.1 ± 0.2	$(3.9 \pm 0.1) 10^{-3b}$

^aMeasured at 1.85 V vs Li.

^bAssuming n equals inserted charge density.

^cMeasured at 1.3 V vs Li.

^dAssuming $n=[\text{Li}]=5$ at. %.

ductance increases by more than five orders of magnitude between 2.6 and 2.0 V vs Li (≈ 10 mC inserted charge). A detailed description of the conductance variation in the double layer region is presented elsewhere.³⁰ The conductance decreases as soon as the phase transition to $\text{Li}_{0.5}\text{TiO}_2$ commences, indicating that the conductivity of this phase is lower than that of TiO_2 in accumulation. This is consistent with the absorption spectra, which show a distinct discontinuity at the onset of the phase transition. Finally, the conductance increases again when charge is injected beyond a composition of $\text{Li}_{0.5}\text{TiO}_2$.

The conductivity σ can be calculated from the measured resistance and the dimensions of the material inside the gap. It is given by $\sigma = W/RLt$, where R is the measured resistance, W is the gap width, t is the film thickness, and L is the length over which the gap is bridged by the film. The electron mobility μ can be calculated with the expression $\sigma = ne\mu$, where n is the electron concentration and e is the elementary charge. The values at the two characteristic points in Fig. 4, i.e., at the maximum and minimum conductances, are collected in Table II. The minimum corresponds to a composition of $\text{Li}_{0.5}\text{TiO}_2$. It should be noted that the corresponding value for the mobility is calculated assuming that *all* injected electrons contribute equally to the conductivity. At the maximum, it is impossible to distinguish between charge compensation by Li^+ in solution (accumulation) and by Li^+ ions in the lattice (solid solution). For comparison, we include data at 2.0 V, i.e., before solid solution formation is likely to occur. All values in Table II are, within experimental error, independent of film thickness and gap width, except for the dense films in the accumulation regime. Since the accumulation layer in dense films does not extend throughout the entire film, the corresponding values in Table II are based on an estimated value of 11 nm for the accumulation layer thickness.¹⁹ Data for mesoporous films are corrected for the porosity, i.e., σ and μ are normalized on the amount of TiO_2 .

It is interesting to analyze in more detail the resistance variation during the phase transition between TiO_2 and $\text{Li}_{0.5}\text{TiO}_2$. Figure 5 shows the measured data in this region for dense films (26 and 50 nm thickness) and for mesoporous films (inset; variable film thickness and gap width). We first look at the dense films. In the intercalation regime the film

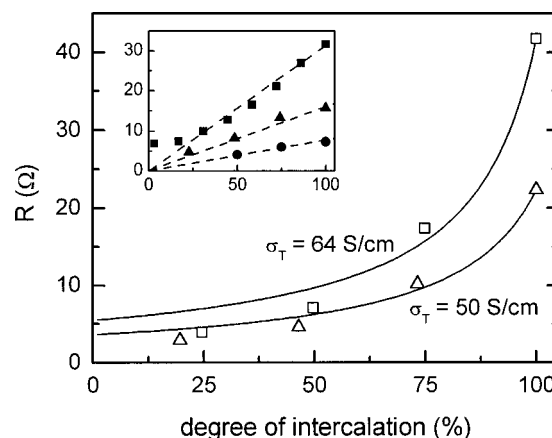


FIG. 5. Resistance vs degree of intercalation for dense films in the intercalation regime. $\square$) 26 nm; $\triangle$) 50 nm. The solid lines are least-square fits of the data to extract the conductivity of the lithium-doped anatase TiO_2 phase, σ_T . The corresponding data for the mesoporous films are shown in the inset. Here, the resistance is proportional to the degree of intercalation and the gap width, W , and inversely proportional to the number of successively applied coatings, c . $\blacksquare$) $W=20 \mu\text{m}$, $c=1$; $\blacktriangle$) $W=10 \mu\text{m}$, $c=1$; $\bullet$) $W=10 \mu\text{m}$, $c=2$.

can be viewed as two single-phase layers stacked on top of each other.¹⁷ In the forward scan, the top layer is $\text{Li}_{0.5}\text{TiO}_2$, which grows at the expense of the underlying lithium-doped anatase TiO_2 layer as more lithium is inserted. In the reverse scan, the stacking order is most likely reversed.¹⁷ The total resistance of the film can be modeled as two parallel resistors describing either phase, the thickness of which is determined by the degree of intercalation. Since the conductivity of the $\text{Li}_{0.5}\text{TiO}_2$ phase is known (Table II), the total resistance can be fitted as a function of inserted charge. This gives the conductivity of the Li-doped anatase phase, σ_T . The resulting fits for the 26 and 50 nm films are shown in Fig. 5 (solid lines). The proposed two-layer model provides a good description of the measured data, yielding an average value of (57 ± 7) S/cm for the conductivity of Li-doped anatase TiO_2 at its estimated solubility limit of 5 at. %.

As indicated in Fig. 6(a), three regions can be distinguished in dense films: “bulk” $\text{Li}_{0.5}\text{TiO}_2$, Li-doped TiO_2 , and the accumulation layer at the surface. One may argue that the decrease of the conductivity in the intercalation regime is caused by a decrease of the amount of charge in the accumulation layer. Although an accumulation layer may be present in both the forward (insertion) and reverse (extraction) scans, the amount of charge inside this layer will be different for both scan directions. This is caused by (i) the slightly different open-circuit potentials during insertion and extraction,^{2,18} and (ii) the different stacking order of the layers for different scan directions, as illustrated in Fig. 6(a).¹⁷ However, the measured resistances during forward and reverse scans are identical. This implies that the measured resistance variations during intercalation cannot be attributed to changes in the space charge at the electrode|electrolyte interface, but instead reflect changes in the combined bulk resistance of the $\text{Li}:\text{TiO}_2|\text{Li}_{0.5}\text{TiO}_2$ layers.

The resistance versus degree of intercalation for the mesoporous films is shown in the inset of Fig. 5. The conduc-

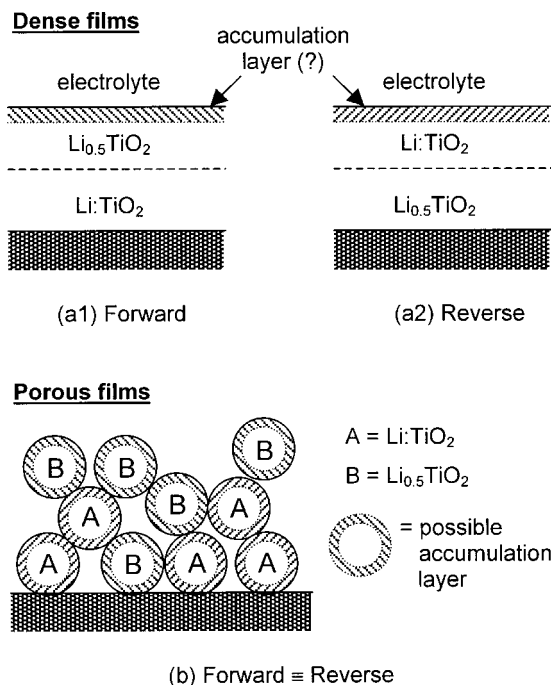


FIG. 6. Illustration of the influence of film morphology on the distribution of the $\text{Li}:\text{TiO}_2$ and $\text{Li}_{0.5}\text{TiO}_2$ phases during lithium intercalation. Note that the extent of the accumulation layer may be different for each phase.

tivity of mesoporous $\text{Li}_{0.5}\text{TiO}_2$ is measured at full intercalation, yielding a value of (0.42 ± 0.04) S/cm. This is significantly lower than that for dense films (cf. Table II) and will be discussed in more detail in the next section. The conductivity of the $\text{Li}:\text{TiO}_2$ phase cannot be readily determined from the inset of Fig. 5 because the extrapolated curves intersect the origin. Instead, the conductivity is measured at 1.85 V vs Li, just above of the $\text{TiO}_2|\text{Li}_{0.5}\text{TiO}_2$ equilibrium potential of ≈ 1.8 V vs Li.^{2,6,18}

A linear increase of R with the degree of intercalation is observed in the inset in Fig. 5. This is not expected for a three-dimensional interconnected network consisting of randomly distributed $\text{Li}_{0.5}\text{TiO}_2$ and $\text{Li}:\text{TiO}_2$ particles.³¹ Percolation theory and general effective medium theory can be used to describe the resistance of a mixture of a well-conducting and poorly conducting particles. Both predict that the resistance in a random system is markedly smaller than the series addition, if the fraction of the conducting phase exceeds a percolation threshold f_c (typically $0.15 < f_c < 0.50$) because above f_c the current chooses the least resistive path. Hence, some degree of order is probably present in the samples studied here. For instance, one can imagine that the $\text{Li}_{0.5}\text{TiO}_2$ phase starts to form at the sides of the gap. Note that this phenomenon would not affect the interpretation of the maximum and minimum conductances observed as these relate to single-phase regions.

The possibility of lithium insertion beyond $x=0.5$ is investigated by providing a stronger driving force for intercalation. This is accomplished by applying potentials below 1.7 V vs Li. In order to rule out possible conduction through a film formed at the electrode surface by electrolyte decomposition (the so-called *solid electrolyte interphase*),^{21,22} experiments were carried out with the standard electrolyte and with

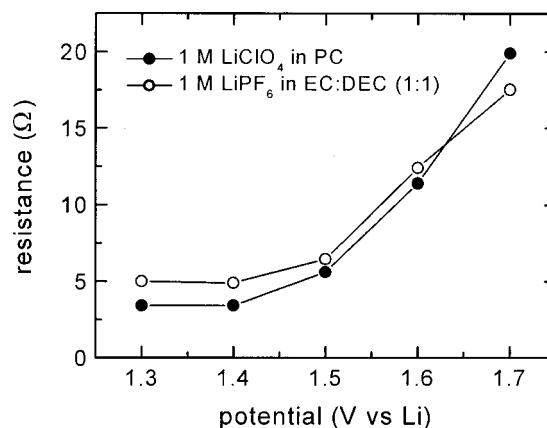


FIG. 7. Resistance vs potential for mesoporous films in two different electrolytes at potentials well below the $\text{TiO}_2|\text{Li}_{0.5}\text{TiO}_2$ equilibrium potential. Both electrolytes yield similar values, and the observed trend is independent of scan direction.

a commercial battery electrolyte (1.0 M LiPF_6 in 1:1 ethylene carbonate/diethylcarbonate, Merck). The film-forming properties of these electrolytes are known to be rather different.³² The results are shown in Fig. 7. The overall trend is that the resistance for both electrolytes increases in the same fashion. The resistance changes are reversible, i.e., when going to 1.7 V after prolonged intercalation at 1.3 V the resistance increases again. The average value for the conductivity is (1.7 ± 0.6) S/cm at 1.3 V vs Li, significantly higher than that for $\text{Li}_{0.5}\text{TiO}_2$ (cf. Table II). As the conductance responds very slowly to potential perturbations it is not related to variable electron accumulation. Hence, it is concluded that lithium insertion beyond $x=0.5$ is possible at potentials below 1.7 V vs Li. Although the trend in Fig. 7 is reproducible, the resistance values should only be interpreted in a qualitative manner. Furthermore, accurate determination of the intercalated charge was not possible due to an anodic contribution from the decomposition layer at the electrode surface. Hence, the true charge associated with the $\text{Li}_{0.5+x}\text{TiO}_2$ data points in Fig. 4 is markedly smaller than shown, and no reliable values for the mobility can be extracted.

IV. DISCUSSION

The electrical conductivity of mesoporous films cannot be directly compared to that of the dense films. The effect of the porous structure on the conductivity can be evaluated with the help of percolation theory and general effective medium theory.^{31,33} This approach was followed by Meulenkaamp for ZnO films having a similar morphology as the mesoporous TiO_2 films studied here.¹⁶ It was shown that the nanostructured morphology leads to an approximately four-fold decrease of the electrical conductivity compared to a fully dense film of the same thickness. The values in Table II are already corrected by a factor of 2 for the porosity. An additional factor of 2 is thus required for a proper comparison between dense and porous films.

According to Table II, the percolation correction leads to a value of 0.84 S/cm for the conductivity of mesoporous

$\text{Li}_{0.5}\text{TiO}_2$. This is an order of magnitude smaller than the conductivity of dense $\text{Li}_{0.5}\text{TiO}_2$ films. An even larger difference is observed for Li-doped TiO_2 and TiO_2 in accumulation. These differences are reflected in the mobilities shown in Table II. Hence, one or more mechanisms slow down charge transport in mesoporous films. This must be associated with *interparticle* transport and surface defects. Indeed, trap-limited charge transport,³⁴ Coulomb repulsion between electrons in adjacent particles,³⁵ and slow tunneling between particles¹⁶ have been proposed in the literature. The conductivity of mesoporous TiO_2 is discussed in more detail elsewhere.³⁰

The importance of the surface is also clear from another observation: the conductivity of (mesoporous) TiO_2 in the accumulation regime depends on the history of the sample. An insertion/extraction cycle induces a two-fold decrease in the conductivity. This is attributed to intercalation-induced chemical changes at the electrode surface²² which can lead to a more negative flatband potential.¹⁷ As a result, less electrons are injected at the same potential and the conductivity decreases. In addition, changes in the dielectric constant of anatase TiO_2 after an insertion/extraction cycle¹⁷ may influence the conductivity. The data presented in Table II on TiO_2 in accumulation are for films not previously subjected to intercalation.

The mobility for dense TiO_2 in accumulation is in good agreement with reported values for microcrystalline anatase, which range from 0.1 to $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.³⁶ This indicates that the films studied are well-crystallized and do not contain a large defect concentration. The optical absorption data pointing to the presence of at least partially delocalized electrons support this conclusion.

Surprisingly, the electron mobility in dense $\text{Li}_{0.5}\text{TiO}_2$ is two orders of magnitude lower. This is consistent with the absence of free-electron absorption in Fig. 3(b), and implies that electrons in $\text{Li}_{0.5}\text{TiO}_2$ behave very differently from those in anatase TiO_2 . The electrical conductivity of dense $\text{Li}_{0.5}\text{TiO}_2$ is found to be $(9.1 \pm 0.2) \text{ S/cm}$. Again the value for the mesoporous films is more than one order of magnitude smaller. Previously reported values for compressed $\text{Li}_{0.5}\text{TiO}_2$ powders are a factor of 3×10^6 lower.² Those measurements were performed *ex situ*, and the low values may be an effect of sample degradation caused by exposure to air. In addition, poor contact between the powder particles in a pressed pellet can also result in anomalously low values for the electrical conductivity.

It is often assumed that the Li^+ -compensating electrons reside in the conduction band, which consists mainly of Ti 3d orbitals. For a composition of $\text{Li}_{0.5}\text{TiO}_2$, this interpretation would lead to a high free-electron concentration of $1.4 \times 10^{22} \text{ cm}^{-3}$. This would certainly induce a Mott transition^{36,37} and metallic conduction. Instead, Figs. 4 and 7 show that an increase of the lithium concentration results in a decrease of the conductivity. Although the simple (nearly-) free-electron picture can be used for low lithium concentrations, a different approach is required in order to understand the electronic structure at high lithium concentrations. Two important aspects should be considered in the discussion: the structural changes that accompany the phase transformation

from anatase TiO_2 (tetragonal) to $\text{Li}_{0.5}\text{TiO}_2$ (orthorhombic), and the position of the Li 2s and Ti 3d energy levels in the band diagram.

According to Cava *et al.* the phase transformation from anatase TiO_2 to $\text{Li}_{0.5}\text{TiO}_2$ does not greatly distort the TiO_2 host lattice.¹ Hence, no dramatic changes in the Ti and O energy levels are expected and a reasonable description of the band diagram can be obtained by simply inserting the Li orbitals at the appropriate position. Lithium has a very low ionization energy and the energy level of its 2s electron is, therefore, expected to lie well above the Ti 3d levels that make up the conduction band. This is generally the case for alkali metals that are incorporated in a transition metal oxide.³⁷ The 2s electrons will subsequently enter the lowest unoccupied energy levels, which are located in the conduction band. This is supported by x-ray photoelectron spectroscopy measurements, which show that Ti^{4+} is reduced to Ti^{3+} upon lithium insertion.¹³

A comparison to work on proton- and lithium-intercalated WO_3 is useful at this stage (see Ref. 27 for an overview of relevant literature data). Crystalline M_xWO_3 shows nonmetallic behavior for x smaller than about 0.2 with σ ranging from 10^{-4} to 10^2 S/cm . Amorphous M_xWO_3 is nonmetallic for all x values studied. Both materials show a strong absorption in the visible part of the spectrum. The optical properties are usually described by small polaron absorption or intervalence charge transfer. This is also a reasonable picture for the main absorption peak of $\text{Li}_{0.5}\text{TiO}_2$ at 725 nm. The origin of the second smaller absorption at smaller wavelengths remains unclear.

The nonmetallic character of $\text{Li}_{0.5}\text{TiO}_2$ remains to be explained, as this is clearly different from crystalline M_xWO_3 . The structural changes during the phase transformation could lead to a decrease in overlap of the Ti 3d orbitals. In combination with narrow bands, this can cause the electrons to become localized on individual Ti atoms.³⁷ However, this picture cannot explain the increase in conductivity when the stoichiometry increases beyond $x=0.5$ (Figs. 4 and 7). The same objection can be made if small polaron formation, as in M_xWO_3 , were assumed to be responsible for the low electron mobility.

The origin of the low electron mobility of $\text{Li}_{0.5}\text{TiO}_2$ can be explained by electron repulsion effects. A well-known manifestation thereof is a Mott–Hubbard splitting of the 3d levels, which leads to a low conductivity for specific values of the free-electron density.³⁷ Small deviations of the electron stoichiometry in $\text{Li}_{0.5}\text{TiO}_2$ would then lead to an increase in the conductivity, as is indeed observed in Fig. 4. Recent work on $\text{Li}_x\text{V}_2\text{O}_5$ also shows complicated variations³⁸ in the electronic conductivity during transitions between the various Li-containing phases. Band structure calculations on $\text{Li}_{0.5}\text{TiO}_2$, similar to those already available for other Li-containing TiO_2 phases,^{20,28,39} should give more insight into the electronic and optical properties of $\text{Li}_{0.5}\text{TiO}_2$ and $\text{Li}_{0.5+x}\text{TiO}_2$.

V. CONCLUSIONS

The resistance changes of dense and mesoporous anatase TiO_2 films during electrochemical intercalation of lithium

could be measured *in situ* by using a special electrode geometry. The combination of the conductivity data with optical absorption spectroscopy has led to a better understanding of the behavior of anatase TiO₂ during lithium intercalation.

Three different regimes can be discerned in the intercalation process. The double layer regime is characterized by injection of electrons and the concomitant formation of an accumulation layer. The injected electrons are free (or nearly free), as evidenced by a large increase in conductivity and the steady increase of absorption with wavelength. In the second regime a phase transformation to Li_{0.5}TiO₂ takes place, and the conductance of the film decreases. The shape of the absorption spectrum changes and the free-electron absorption features are replaced by two pronounced absorption peaks near 440 and 725 nm, indicating localized electrons. In addition, the overall absorption increases significantly and visual coloration of the films is observed. The low conductivity of Li_{0.5}TiO₂ may be explained in terms of electron repulsion effects. In the third regime lithium is inserted into Li_{0.5}TiO₂, resulting in an overall composition of Li_{0.5+x}TiO₂. The conductivity increases again, indicating that a higher band with good conduction properties is filled.

The optical and electrical changes in mesoporous and dense TiO₂ films during lithium intercalation follow the same general trend. However, absolute conductivity values for mesoporous films are much smaller than those for dense films. This is partly due to percolation effects in the mesoporous structure. More important factors, however, are the presence of a barrier for interparticle charge transport, and the possible role of surface defects. The exact cause for the much lower conductivity in porous films is unclear, and calls for further investigation.

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