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Ab initio study on the topological Li insertion in titanium oxide

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Abstract

Lithium insertion into anatase was studied by XRD, XPS and ab initio calculations. Lithium insertion in anatase was carried out by n-butyllithium and the product was analyzed by XRD and XPS. A distortion of anatase cell by the lithium insertion and removal was estimated by the ab initio periodic pseudo-potential calculations. As a result, a crystallographic transition from tetragonal to orthorhombic along with a considerable hysteretic change of the cell volume were estimated, which is well consistent with the previously reported XRD cell dimensions. In the lithium-removal process, the wide plateau in calculated cell volume was observed for Li_xTiO_2 where lithium uptake x ranges from 0.25 to 1. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Lithium ion secondary battery is widely applied to portable telephones, computers, video cameras, and so on because of its high energy density and rechargeability. It is expected to be applied to not only portable electric equipments, but also as a power source in electric vehicles. As for the cathode materials, many transition metal oxides, especially lithium cobalt oxides and lithium manganese oxides have been actively studied, and the former have been developed for practical use. As we know, the specific energy more than 180 W h kg^{-1} and the cycle life more than 500 times are two of the major requirements for a high energy density battery [1]. Now, to achieve the targets, a topochemical lithium insertion/extraction cycle is required which will not result in any considerable deformation or transition of the host crystal. However, the relationship between the topochemical process and the crystal structures of the host materials has not yet been clarified.

Titanium oxide is an inexpensive and lightweight material which has favorable sites for Li insertion in its structure. Considering these advantages, titanium oxide is expected to be used as a cathode material for the lithium ion secondary batteries. Titanium oxide has various crystal

types [2] such as, rutile, anatase, brookite, $TiO_2(B)$, ramsdellite type $Li_2Ti_3O_7$, spinels, and so on. The lithium insertion reaction into these hosts has been investigated [3–8]. Zachau-Christiansen et al. [7,8] reported the electrochemical insertion of Li in anatase and rutile. As a result, the Li uptake was found to be 0.5 in anatase, whereas no insertion reaction was detectable for rutile cells. Neat and Macklin [9] carried out charge/discharge cycling using anatase and rutile as a cathode material at 120°C. In the first discharge, anatase and rutile showed quite high energy densities of 565 and 500 W h kg^{-1}, respectively. However, the anatase form demonstrated poorer capacity retention than that of rutile. Bonino et al. [10] reported that the lithiated anatase material Li_xTiO_2 has been cycled in an electrochemical cell over the range of x from 0.15 to 0.45.

On the other hand, theoretical studies have been done on the titanium oxide polymorphs and on the lithium insertion reaction using computational techniques. Milman [11] compared the calculated energies and structures of all the polymorphs of TiO_2 using the CASTEP package. Stashans et al. [12] studied lithium insertion into rutile and anatase by quantum chemical Hartree–Fock calculations. The results predicted a higher possibility of lithium intercalation in the anatase structure than that in rutile. Nuspl et al. [13] analyzed the lithium insertion in anatase and $TiO_2(B)$ from approximate crystal orbital calculations. It was suggested that a further insertion of Li into TiO_2

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beyond a stoichiometry of $Li_{0.5}TiO_2$ became rather difficult because it led to additional repulsive Li–Li contacts.

The lithium insertion reaction in titanium oxides should be studied by ab initio calculation which could make the development of active cathode material efficient and economical because of its two advantages; (1) Calculated results are accurate, (2) This calculation needs only the crystallographic data of the host material.

In this study, optimal structures of anatase and the corresponding lithium titanium oxide Li_xTiO_2 were determined by the ab initio calculation, then the calculated cell deformation was discussed. The chemical state of Ti in the Li_xTiO_2 sample were analyzed by X-ray photoelectron spectroscopy (XPS).

2. Experimental and calculation

2.1. Preparation of the lithium titanium oxide

Lithium insertion was carried out as follows; Anatase powders (Wako, 99.9% purity) were dispersed in hexane (Wako, 97% purity), then the equivalent amount of *n*-butyllithium (*n*-BuLi) hexane solution (Nakarai Tesque, 1.6 mole dm^{-3}) was added, stirred for 24 h, filtrated, and then washed by ethanol (Wako, 99.5% purity). The above process was carried out in Ar atmosphere. The samples were vacuum dried and powdered. The products were characterized by XRD and XPS. X-ray diffraction patterns of the samples were recorded on a Rigaku RAD-X system using monochromatized Cu K_α radiation. Atomic concentrations and chemical states of the products were analyzed by XPS, Ulvac-PHI ESCA-5600ci. Monochromatized Al K_α X-rays were applied using an electron flood gun. The pressure was kept under 1×10^{-7} MPa. Energy reference was done by adjusting the C(1s) peak from adventitious carbon layer at 284.6 eV.

2.2. Quantum chemical calculations

Pseudopotential plane-wave-based codes, CASTEP (MSI), was used for all geometry optimizations. It is based on the efficient minimization of the total energy of the many-electron periodic system within the DFT formalism. Three-dimensional periodic boundary conditions were imposed. Exchange-correlation effects were taken into account within GGA in the Perdew–Wang formulation [14]. Non local potentials were selected for all species, Ti, O and Li.

The kinetic energy cut off value was 330 or 450 eV as described in Section 3. For all calculations, the total charge of the cell was set at neural. An O2 workstation (Silicon Graphics) was used.

3. Results and discussion

3.1. Crystal deformation by the lithium insertion

The equivalent amount of *n*-BuLi was added to the TiO_2. However, the Li/Ti ratio of the product was determined at 0.49, which means about a half of Li in the solution was inserted in TiO_2. The lithium uptake is consistent with the value by an electrochemical insertion [8]. Fig. 1 shows XRD patterns of TiO_2 and the $Li_{0.49}TiO_2$ produced by the chemical lithium insertion. The XRD pattern of TiO_2 shows strong anatase peaks and weak rutile peaks. No considerable difference in peak position and peak intensity was observed between the two patterns which were taken before and after the lithium insertion. It suggests that observable crystal transformations and additional precipitations did not occur during the reaction.

Chemical states of Ti in the samples were analyzed by XPS. Fig. 2 shows Ti(2p) peaks of the samples before and after the lithium insertion. The $Ti(2p_{3/2})$ and $Ti(2p_{1/2})$ peaks of the TiO_2 sample were observed at 458.6 and 465.6 eV, respectively. The shape of the former peak changed obviously after the Li insertion even though the latter peak did not show any obvious change in shape. A shoulder peak was observed with a slightly higher binding energy than the dominant $Ti(2p_{3/2})$ peak in the spectrum of $Li_{0.49}TiO_2$. The $Ti(2p_{3/2})$ peak was separated into two component peaks by a curve-fitting calculation using a Gaussian–Lorenzian curve shape, and the binding energies of the two component peaks were determined at 457.5 and 456.2 eV. The chemical shift towards lower binding energy may be attributed to the reduction of Ti from tetravalent to trivalent state that resulted from the lithium insertion. This deduction is acceptable by considering previously reported binding energy values for TiO_2, TiO and Ti metal at 458.8, 455.1 and 454.1 eV, respectively [15]. The observed two component peaks are in between the first and the second values which corresponded to tetravalent and divalent state, respectively.
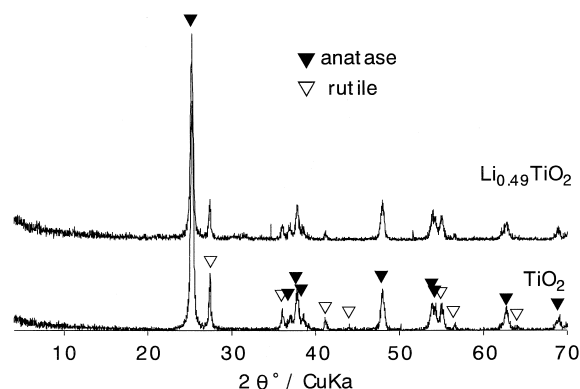

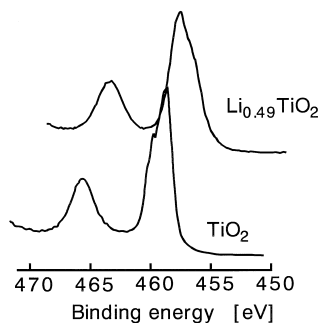Fig. 1. XRD patterns of the TiO_2 and the $Li_{0.49}TiO_2$ samples.

Fig. 2. Ti(2p) spectra of the TiO_2 and the $Li_{0.49}TiO_2$ samples.

3.2. Crystal deformation of anatase due to the lithium insertion

The validity of the ab initio calculation used in this study towards titanium oxides was verified as mentioned in Section 4 before applying it for the estimation of the crystal deformation due to the lithium insertion. First, the optimization of three TiO_2 polymorphs such as rutile, anatase and brookite were carried out and the results were compared with the XRD crystal data (Table 1). The cutoff energy level affected the accuracy of the calculated cell parameters. The increase of the cutoff energy from 330 to 450 eV improved the accuracy significantly. The improved accuracy was comparable to that using empirical calculations by le Roux and Glasser [16], and the calculated lattice parameters match with the experimental values within an error range of 0.7%. Calculated relative energies of the three polymorphs were as follows: brookite 17 kJ/mol Ti, anatase 15 kJ/mol Ti and rutile 0 kJ/mol Ti. The energy order fits with the well known experimental stability order of the above three phases, brookite < anatase < rutile.

Next, the deformation of the anatase structure was estimated by the following procedure. A unit cell of anatase was built on the basis of the XRD crystal data. The

formula of the cell was Ti_4O_8 and it has four Li absorption sites. Then Li atoms were added into the cell one by one followed by an optimization of the cell dimensions until the whole sites were occupied by Li. Then all Li atoms were inversely removed from the cell one by one followed by the optimization of the cell dimensions.

The calculated cell dimensions varied with the amount of lithium (x) (Fig. 3). Axial length of a and b increased gradually with the lithium insertion below $x = 0.75$, following a locus. This result is consistent with the fact that XRD patterns of anatase and $Li_{0.7}TiO_2$ were essentially the same [9]. However, when the amount of lithium reached the theoretical limit of $x = 1$, the cell transferred from tetragonal to orthorhombic; the b axial length increased, whereas the a decreased. A abrupt decrease of c axial length was also observed in this range. Considerable hysteretic change of the axial length was observed between the insertion and the removal processes. In the removal process, orthorhombic cell was maintained until $x = 0.25$. After the insertion/removal cycle, axial length of a and b was almost the same as those of anatase; however, c shortened by approximately 2%. This behavior of the cell dimensions, i.e., the cell expansion along a and b axis and shrinking along c-axis, is consistent with XRD crystal data by Zachau-Christiansen et al. [8] plotted in Fig. 3.

Fig. 4 shows the hysteretic variation of unit cell volume with lithium insertion and removal process. In the insertion process, a large change of the cell volume was observed at $x = 0.75$. This large volumetric change and the transition of the cell may cause the poor capacity retention of anatase [9]. In the removal process, a plateau was observed over the range of $1 > x > 0.25$. It must be noted that, in the
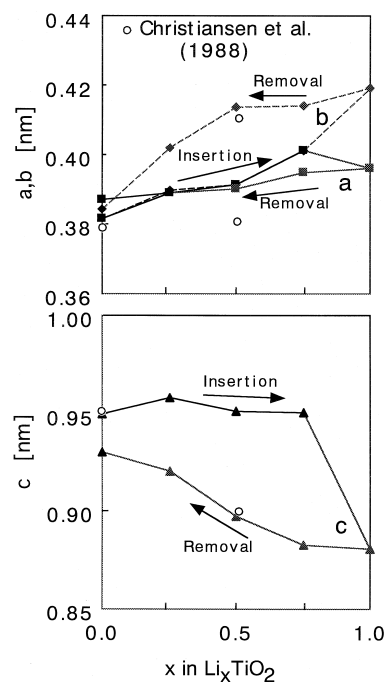
Table 1
Calculated cell dimensions of rutile, anatase and brookite

	Experimental	330 eV[a]		450 eV[a]	
		Calculated	Error[b]	Calculated	Error[b]
Rutile					
a (nm)	0.4594[c]	0.4605	0.24	0.4590	−0.09
c (nm)	0.2959[c]	0.2981	0.74	0.2981	0.74
Anatase					
a (nm)	0.3785[c]	0.3776	−0.24	0.3813	0.74
c (nm)	0.9514[c]	0.9486	−0.29	0.9496	−0.19
Brookite					
a (nm)	0.9250[d]	0.9156	−1.02	0.9191	−0.64
b (nm)	0.5460[d]	0.5433	−0.49	0.5472	−0.22
c (nm)	0.5160[d]	0.5128	−0.62	0.5196	0.70

[a] Kinetic energy cut off.
[b] (Calc. − Exp.)/Exp. × 100.
[c] Cromer and Herrington [17].
[d] le Roux and Glasser [16].

Fig. 3. Calculated cell dimensions of Li_xTiO_2 plotted against lithium x.
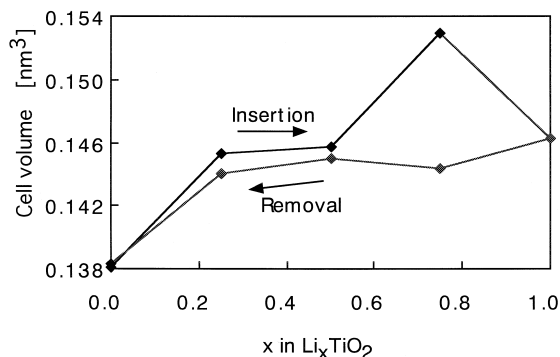
Fig. 4. Calculated cell volume of Li$_x$TiO$_2$ plotted against lithium x.

range of $1 > x > 0.25$, the variation of the cell volume was smaller than 2% because of the compensating changes of b and c axial length (Fig. 3). Therefore, the lithium removal in this range is not topotactic, however, the volumetric behavior is favorable because it may prevent a rapid deterioration of the cathode due to the small total volume change. Therefore it is expected that the orthorhombic Li$_x$TiO$_2$ can be used as cathode over the range of $0.25 < x < 1$.

We did not execute the spin polarized calculation for all calculations in the present work. Now, we compared the cell dimensions calculated with and without the spin polarizing effect. A considerable difference was observed between the two cases. In the former case, the cell dimensions, (a, b and c) have the values 3.8670, 3.8906 and 9.5652, respectively; whereas in the latter case they were 3.8893, 3.8990 and 9.5804, respectively. The differences of a, b, c observed between two cases were 0.99, 0.58 and 0.16%, respectively. From this point we plan to perform a rigorous calculation considering the spin polarizing effect in the next step of this study.

4. Conclusion

Lithium insertion into anatase was studied by the ab initio calculation. Lithium insertion in anatase was carried out by n-butyllithium and the product was analyzed by XRD and XPS. The lithium uptake was about a half of the theoretical limit. No obvious crystal deformation was shown, however, the chemical shift of Ti(2p) peak towards lower energy side was observed, which is attributed to the reduction of Ti from tetravalent to trivalent.

Cell dimensions of the three polymorphs of TiO$_2$, anatase, rutile and brookite were well reproduced by the ab initio calculation, and then the distortion of anatase cell by the lithium insertion was calculated. As a result, the crystallographic phase transition from tetragonal to orthorhombic was estimated, which is well consistent with the previously reported XRD cell dimensions. Considerable hysteretic change of the cell volume and dimensions were observed. In the removal process, the wide plateau in calculated cell volume was observed over the range of $1 > x > 0.25$.

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