[논 문] 한국재료학회지
Korean Journal of Materials Research
Vol. 14, No. 9 (2004)

Synthesis of Lithium Titanate Whisker Using Ion-Exchange of Acid Treatment

Myeong-Heon Um† and Jin-Sik Lee*

DepartmentofAdvancedMaterialsChemicalTechnology,ChonanNationalTechnicalCollege,
Chonan 330-717, Korea
*R & D Cent, VITZROCELL Co., Ltd, Dugok-Li, Shinam-Myon, Yesan-Gun, Chung-Nam, 340-861, Korea

(2004년 7월 23일 받음, 2004년 9월 2일 최종수정본 받음)

Abstract Lithium titanate whisker($Li_xTi_4O_9$) was prepared by an ion-exchange reaction. To this end, the initial material, potassium tetratitanate ($K_2Ti_4O_9{\cdot}nH_2O$) was prepared by calcination of a mixture of K_2CO_3 and TiO_2 with a molar ratio of 2.8 at 1050°C for 3 h, followed by boiling water treatment of the calcined products for 10 h. Fibrous potassium tetratitanate could be transformed into layered hydrous titanium dioxide ($H_2Ti_4O_9{\cdot}nH_2O$) through an exchange of K^+ with H^+ using 0.075 M HCl. Also, lithium titanate whisker was finally prepared as Li^+ and H^+ ions were exchanged by adding 20 mL of a mixture solution of LiOH and $LiNO_3$ to 1g whisker and stirring for 5~15 days. The average length and diameter of the $Li_xTi_4O_9$ whiskers were 10~20 μm and 1~3 μm, respectively.

Key words ion exchange(Host-Guest) reaction, lithium titanate whisker.

1. Introduction

Cathode materials for lithium secondary cells are expected as a high energy density power source for many portable electronic apparatus or as a load levelling battery recently. Especially, intercalation compounds with a spinel structure (Fd3m) are promising materials as the cathode with high energy density.[13] Generally, lithium spinel oxides LiM_2O_4 (M: transition metals) suitable for the cathode are limited to the those with a normal spinel in which the lithium ions occupy the tetrahedral sites (8a) and the transition metal ions reside at the octahedral sites(16d). In an inverse spinel, however, a part or half of the M ions in the 16d sites displace the lithium ions in the 8a sites and prevent easier diffusion of lithium ions from 8a to other 8a sites via vacant octahedral 16c sites.[3] The lithium intercalation has previously been demonstrated for LiM_2O_4 (M = Ti, V, Mn) with a capacity of one additional Li per formula unit at room temperature.[47] Colbow et al[8] showed that cells using $Li_4Ti_5O_{12}$ as a cathode showed good reversibility and discharge capacity. Ohzuku et al[9] reported $Li_4Ti_5O_{12}$ is a zero-strain insertion material, and the results of electrochemical charging and discharging cycle tests of $Li/Li_4Ti_5O_{12}$ cell seems promising for cathode materials. It is well known fact that $Li_xTi_4O_9$ material has the similar stable sheet structure of $[Ti_4O_9^{2-}]_n$ in a form of whiskers, and such multilayered structure promotes insertion/ extraction of certain metal ions. Further, it is found to be highly selective for Li^+ and the ions can be inserted and extracted relatively at ease.[10] Compared to 3-D structure of a defect spinel oxides $Li_4Ti_5O_{12}$, the whisker has a larger capacity of insertion and extraction of Li^+ ions and thus it opens possibility of application of the whiskers as the active materials in rechargeable lithium cells.

These titanate derivatives have been reported to be formed by such methods as calcination, flux, melt, hydrothermal treatment, KDC(Kneading Drying Calcination) and so on.[1015] It is, however, difficult to produce layered hydrous titanium dioxide and alkali metal titanates with the aid of existing methods.[21] In this respect, the ion-exchange (host-guest) reaction method, where a relatively large molecule, atom or ion (host) in the host framework is substituted with a small molecule, atom or ion (guest) is one of the promising production methods.[16,17] Actually, potassium octatitanate $K_2Ti_8O_{17}$ has been prepared by hydrolysis of $K_2Ti_8O_9$ followed by thermolysis[18,19] and host-guest reaction followed by dehydration.[20,21]

However, these existing studies have not been done from the process engineering points of view, and accordingly, detailed experimental conditions to form octatitanate with

†E-Mail : mhum@cntc.ac.kr

high reproducibility have not been established.

In the present work, we tried to investigate the production of both layered hydrous titanium dioxide and lithium titanate whisker($Li_xTi_4O_9$) with a spinel structure with the help of the ion-exchange reaction method. Experimental conditions were searched for to form these titanate derivatives with high reproducibility and reliability.

2. Experimental Procedure

Fig. 1 shows the flow chart for the synthesis of $Li_xTi_4O_9$ whisker. The starting materials, K_2CO_3 and TiO_2 (rutile), for the syntheses of hydrous titanium dioxide ($H_2Ti_4O_9 \cdot nH_2O$) and $Li_xTi_4O_9$ whisker, were commercially available chemicals of the first grade with purities of 99 and 99.5%, respectively.

A mixture of K_2CO_3 and TiO_2(rutile) with a prescribed molar ratio of 2.8 was prepared by mixing them in a ball mill with added acetone and drying the resultant slurry. The mixture of K_2CO_3 and TiO_2 was then calcined at 1050°C for 3h. The calcined product was composed of potassium di- and tetra-titanate. To get pure potassium tetratitanate which can be transformed into a series of titanate derivatives, the calcined product was agitated in a boiling water for 10 h. By this treatment, dititanate could be converted to tetratitanate effectively. The characterization of potassium di- and tetra-titanate was made by means of XRD and EDS.

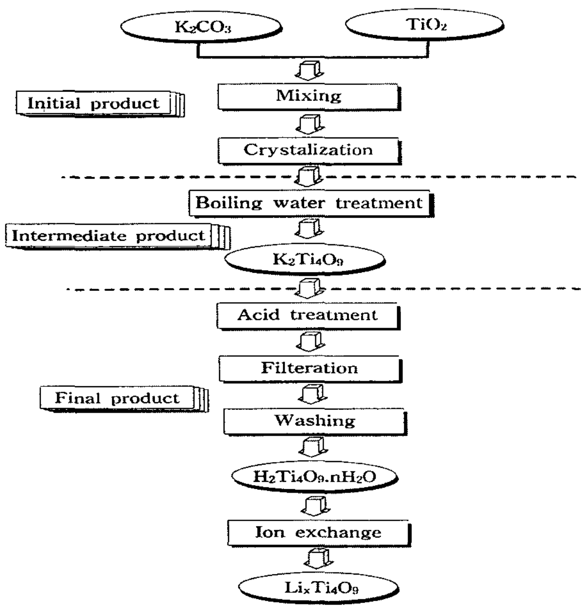


Fig. 1. Flow chart for the synthesis of $Li_xTi_4O_9$ whisker.

Next, we tried to get layered hydrous titanium dioxide ($H_2Ti_4O_9 \cdot nH_2O$) by an exchange of K^+ in fibrous potassium tetratitanate ($K_2Ti_4O_9 \cdot nH_2O$) with H^+ using HCl. To prepare layered hydrous titanium dioxide selectively, HCl treatment conditions, i.e., the concentration of HCl and treatment times, were searched for and clarified. The time courses of the molar ratio of Ti to K (Ti/K) and the amount of K extracted during the acid treatment were measured by ICP and AA analyses of the filtrate and filter cake. The amount of hydrate in $H_2Ti_4O_9 \cdot nH_2O$, i.e., the value of n, was determined by means of a TG/DTA analysis.

$Li_xTi_4O_9$ whisker is finally prepared as H^+ and Li^+ ions are exchanged and this was done by adding 20 mL/(1 g whisker) of a mixture solution of LiOH and $LiNO_3$ and stirring for 5~15 days, and 1M HCl solution was added in order to increase the amount of Li^+ ion exchanged. The mixture solutions were made by different combinations of 0.1~2.0 M LiOH and 1M $LiNO_3$. The amount of Li^+ ion exchanged was determined by ICP(Baird PSX-18, U.S.A) analysis on the whisker residue after washing with deionized water, vacuum filtration and drying over 24 hrs at 110°C. All products were checked by X-ray diffraction analysis(CuKα radiation) and their thermal properties were determined by TGA for the range of 25°C up to 1,000°C with an incremental of 10°C/min.

3. Results and Discussion

3.1 Initial product

Fig. 2 shows the X-ray diffraction pattern and SEM observation results of the calcined products that were obtained during the course of the synthesis. An XRD pattern of the initial calcined products exhibited a mixture composed of potassium di- and tetra-titanates and unidentified species. From a SEM image of the calcined products, both calcined products were of fiber-shape, though the shape was not smooth. As shown in Fig. 3, according to the chemical analysis of the calcined products using an energy dispersion spectrometer (EDS), the compositions of TiO_2 and K_2O were 73.07 and 26.93%, respectively.

The molar ratio of TiO_2 to K_2O was estimated to be 3.2, which also implies that the calcined products were composed of potassium di- and tetra-titanates. Thus, further treatments are necessitated to get pure potassium tetratitanate fibers which can be transformed into a series of derivatives.

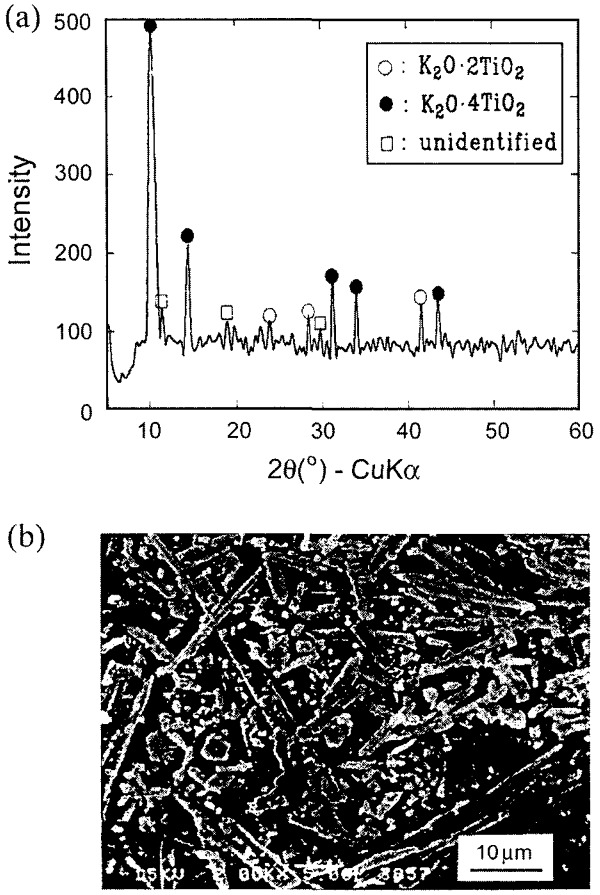
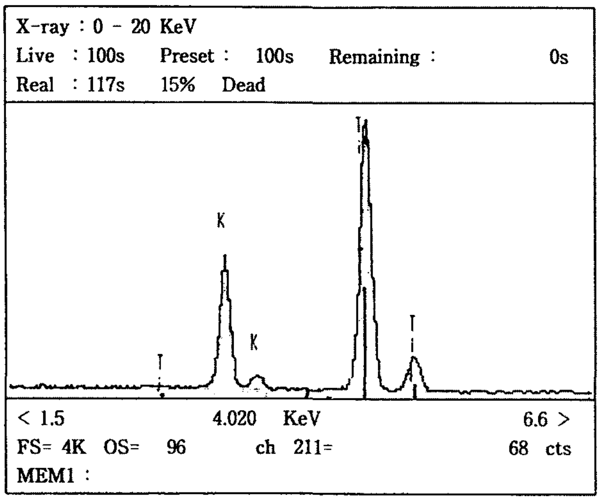


Fig. 2. X-ray diffraction pattern(a) and scanning electron micrographs(b) of initial calcined product.



Composition	TiO_2	K_2O	remark
%	73.07	26.93	mole ratio of TiO_2/K_2O=3.2

Fig. 3. Chemical analysis of the calcined products using an energy dispersion spectrometer(EDS)

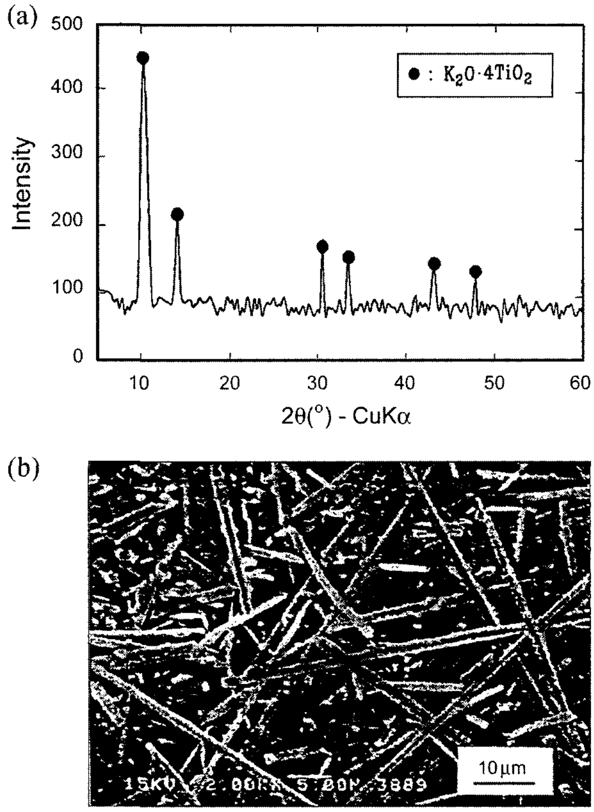


Fig. 4. X-ray diffraction pattern (a) and scanning electron micrographs(b) of intermediate product.(Fixed cond. : Boiling water treatment : 10 hrs)

3.2 Production of potassium tetratitanate (Intermediate product)

A mixture of the above calcined products was agitated in a boiling water for 10h to convert dititanate to tetratitanate effectively. Afterwards, it was filtered and dried at 110°C for 24 h. Fig. 4 shows the X-ray diffraction pattern and SEM observation results of the intermediate products, $K_2Ti_4O_9$.

The XRD pattern of the resultant fibrous particles definitely exhibited only potassium tetratitanate. This determination coincided well with the result of EDS analysis, whereat the molar ratio of TiO_2 to K_2O was determined to be 4.14, a value close to a theoretical value (4.0). According to SEM image of potassium tetratitanate fibers prepared by the above treatment, the average length and diameter of the fibers were estimated to be 23.5 μm and 1.1 μm, respectively.

3.3 Production of layered hydrous titanium dioxide ($H_2Ti_4O_9 \cdot nH_2O$)

A trial was made whether fibrous potassium tetratitanate prepared thus, could be transformed into layered hydrous titanium dioxide ($H_2Ti_4O_9 \cdot nH_2O$) through an exchange of K^+ with H^+ from HCl.

3.3.1 Effects of treatment time and concentration of HCl

Fig. 5 shows the time dependences of the molar ratio of Ti to K (Ti/K) and the amount of extracted K during the HCl treatment at various HCl concentrations.

They were measured by ICP analyses of filtrate and filter cake of HCl treated suspension. As the concentration of HCl increases to 0.075 molar, the molar ratio of Ti to K (Ti/K) gradually increases. Conversely, with increasing HCl concentration above 0.075 molar, the ratio tends to decrease. This is ascribed to the fact that Ti comprising the structure of the titanate as well as K^+ ion start to be extracted by HCl with an increase in its concentration. Fig. 6 indicates the time course of the XRD patterns of the acid treated $K_2Ti_4O_9$ powders at various levels of acid (HCl) concentration.

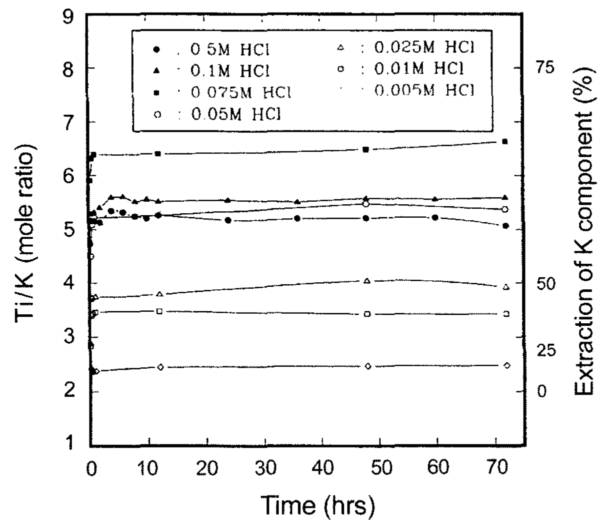


Fig. 5. Time dependence of Ti:K molar ratio extracted from $K_2Ti_4O_9$ under various acid concentrations.

The samples were prepared by drying HCl treated $K_2Ti_4O_9$ at 110°C for 24 h. The Bragg angle (2θ) here ranged from 7 to 15°. As K^+ is exchanged by H^+ and water is added, the main peak on the XRD pattern tends to shift to the right. Such a shift coincides well with th result by Sakaki and Fujiki.[20]

At 0.1 molar or more, fibrous shapes are destroyed by the treatment even for 1 h. Thus, to produce layered hydrous titanium dioxide, the acid concentration must be lower than 0.075 molar.

3.3.2 Effect of acid treatment times

Fig. 7 shows the variation of extraction percentages of K with the treatment times during the treatment with a 0.075 molar HCl solution. Exceeding five times of acid treatment, all of K^+ ions can approximately be removed, and the treatment for five times is judged to be sufficient.

Actually, the XRD patterns of the product samples after the 1st, 3rd, 5th and 7th treatments, exhibited $H_2Ti_4O_9 \cdot nH_2O$. When $K_2Ti_4O_9$ was treated with 0.075 M HCl for

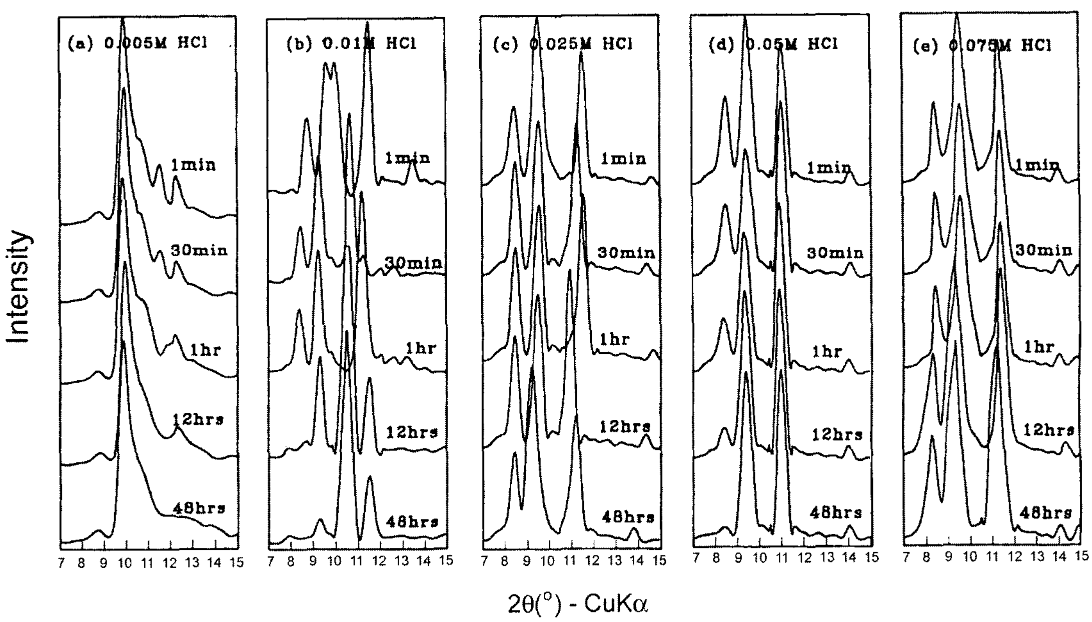


Fig. 6. XRD patterns of various products prepared through an acid treatment of $K_2Ti_4O_9$ under various acid concentrations and treatment times.

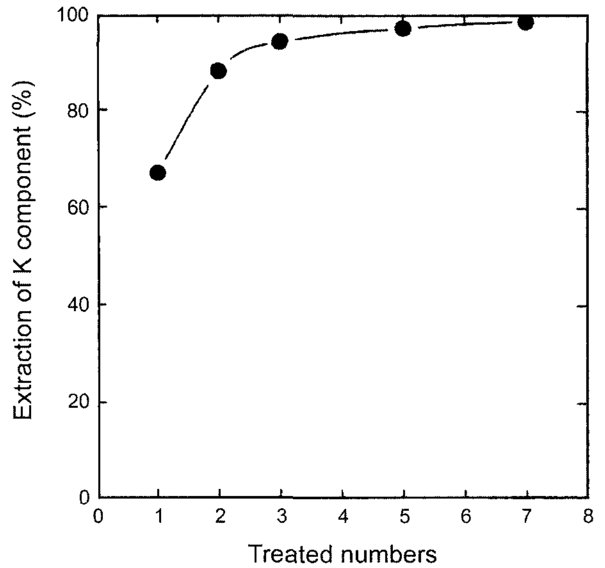


Fig. 7. Variation of extraction percentage of potassium with treatment times.

1 hr and repeating the treatment for five times, practically all of the K^+ ion was exchanged by H^+ ion. This treatment resulted in formation of $H_2Ti_4O_9$ as seen by Fig. 8 and the corresponding length was approximately 20~30 μm.

3.4. Production of lithium titanate whisker, $Li_xTi_4O_9$

$Li_xTi_4O_9$ whisker is finally prepared as H^+ and Li^+ ions are exchanged and this was done by adding 20 mL/(1 g whisker) of a mixture solution of LiOH and $LiNO_3$ with stirring for 5~15 days, and 1 M HCl solution was added in order to increase the amount of Li^+ ion exchanged.

Percent conversion of $H_2Ti_4O_9$ to $Li_xH_{2-x}Ti_4O_9$ are shown in Table 1.

As it can be easily seen from the table that the highest conversion to $Li_xH_{2-x}Ti_4O_9$ whisker occurred when treated with 1M LiOH solution only and the pH at this point was 12.3.

Table 2 shows the percent conversion to $Li_xH_{2-x}Ti_4O_9$ whisker and its dependence to different concentrations of LiOH and treatment time.

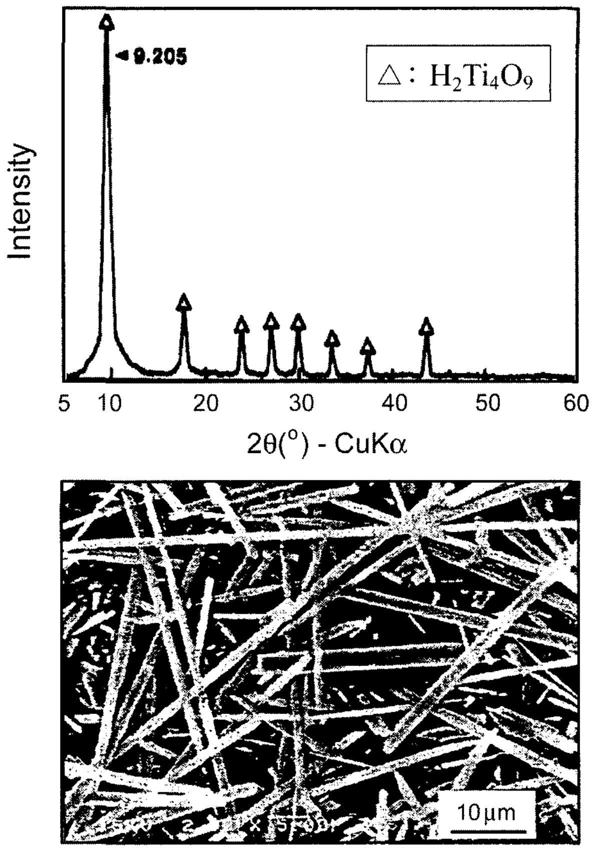


Fig. 8. X-ray diffraction pattern and scanning electron micrograph of $H_2Ti_4O_9$ whisker by boiling water treatment and acid treatment.

Table 1. Effect of mixing ratio for the mixed solution of 1 M $LiNO_3$ and 1M LiOH

	1M $LiNO_3$ only	Mixed solution (1M $LiNO_3$: 1M LiOH) 3:1	2:2	1:3	1 M LiOH only
Conversion (%)	3	30	38	40	44
pH	6.8	12	12	12.2	12.3

As the result it was found that the percent conversion increased as concentration of LiOH increased and/or as treatment time increased and pH decresed. The X-ray diffraction patterns of the three samples obtained by

Table 2. Effect of concentrations of LiOH and treatment time for Li^+ and H^+ ion-exchange

Treatment time (day)	Concentrations of LiOH solution									
	0.1M		0.5M		1.0M		1.5M		2.0M	
	Conversion (%)	pH	Conversion (%)	pH	Conversion (%)	pH	Conversion (%)	pH	Conversion (%)	pH
5	8	11.9	38	12.1	44	12.3	50	12.7	56	13.0
10	10	11.8	39	12.0	46	12.2	52	12.6	58	12.9
15	28	11.6	42	11.8	49	12.0	55	12.5	62	12.8

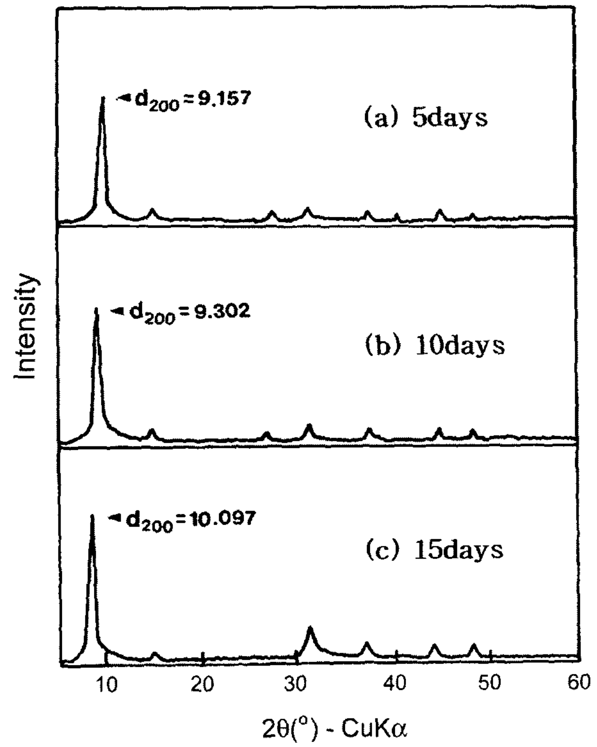
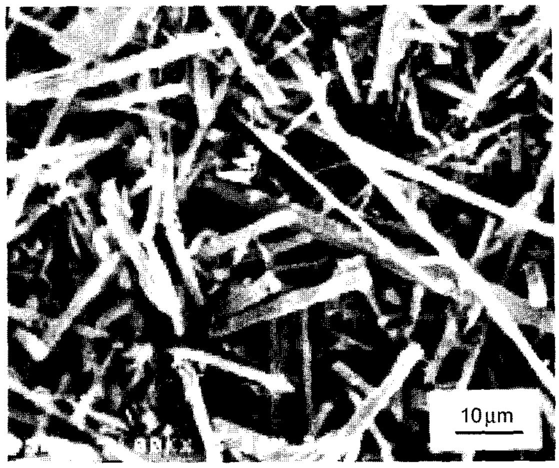
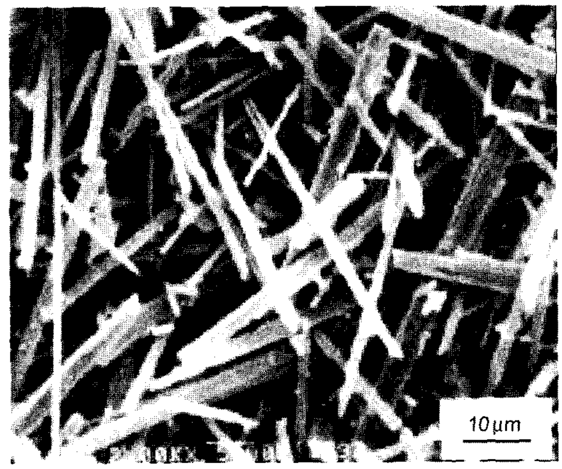


Fig. 9. X-ray diffraction patterns for the investigation of the effect of treatment time on the ion exchange reaction at 1.5M LiOH solution. (a) $LiHTi_4O_9$ (b) $Li_xTi_4O_9$



(a) $LiHTi_4O_9$



(b) Li_xTi_9O

Fig. 10. Scanning electron micrographs of $LiHTi_4O_9$ and $Li_xTi_4O_9$ synthesized by ion exchange reaction at 2.0 M LiOH solution.

treating with 2.0 M LiOH solution for 5, 10, and 15 days are shown in Fig. 9.

During the ion-exchange reaction, Li^+ and H_3O^+ ions are inserted to $H_2Ti_4O_9 \cdot nH_2O$, and correspondingly, the interlayer spacings, represented by the d_{200} reflections, increased from 9.157 to 10.097Å as shown in Fig. 9. This swelling effect disappears as the $Li_xH_{2-x}Ti_4O_9$ whiskers were vacuum dried at 100°C for 3 hrs, in all three cases. Fig. 10 shows SEM images of $LiHTi_4O_9$ and $Li_xTi_4O_9$ whiskers, where the average length and diameter of the whiskers are 10~20 μm and 1~3 μm, respectively.

4. Conclusion

Pure $K_2Ti_4O_9 \cdot nH_2O$ could be prepared by calcination of a mixture of K_2CO_3 and TiO_2 with a molar ratio of 2.8 at 1050°C for 3 h, followed by a boiling water treatment of the calcined products (mixture of potassium di- and tetra-titanate) for 10 h. The average length and diameter of $K_2Ti_4O_9 \cdot nH_2O$ fibers were estimated to be 23.5 and 1.1, respectively. Fibrous potassium tetratitanate could be transformed into layered hydrous titanium dioxide ($H_2Ti_4O_9 \cdot nH_2O$) through an exchange of K^+ with H^+ from HCl. To prepare layered hydrous titanium dioxide, however, all of K^+ ions must be substituted with H^+ ions with the host framework $[Ti_4O_9^{2-}]_n$ kept sheet-like shape. Accordingly, both the acid concentration and the treatment time in the acid treatment were important controlling factors. It has been found that treatment for five times with a 0.075 molar HCl solution effectively yields a layered $H_2Ti_4O_9 \cdot nH_2O$.

$Li_xTi_4O_9$ whisker is finally prepared as H^+ and Li^+ ions are exchanged and this was done by adding 20 mL/(1 g whisker) of a mixture solution of LiOH and $LiNO_3$ and stirring for 5~15 days, and 1 M HCl solution was added in order to increase the amount of Li^+ ion exchanged. The average length and diameter of $LiHTi_4O_9$ and $Li_xTi_4O_9$ whiskers were 10~20 μm and 1~3 μm, respectively.

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