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Room temperature hydrogen uptake of titanate nanotube powder with different H_2O and sodium contents synthesized by a hydrothermal methodin aqueous NaOH solution

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Titanate nanotube powders with high specific surface area for hydrogen storage were synthesized by alkaline hydrothermal treatment of a TiO₂ powder at 150 °C for 48 hrs. With controlling contents of H₂O and Na⁺ in synthesized titanate powders, via ion-exchanging and drying processes, their hydrogen uptake characteristics were evaluated. The titanate nanotube powders showed an increase in the specific surface area with the decreases in Na⁺ content by the ion-exchanging process and in H₂O content by drying processes, but in reverse an decrease in that with severe ion-exchanging or over-drying at high temperature. Their hydrogen uptake increased with decreasing H₂O contents in the powders with appropriate Na⁺ content only under no changing in the particle shape. Therefore, the powders with controlled H₂O and Na⁺ contents had high hydrogen uptake of 2.21 wt% at 90 atm due to proper support of Na⁺ for interlayer distance in multi-walled tube typed titanate particle.

Key words: Titanate nanotube, Hydrogen uptake, Alkaline hydrothermal process, Adsorption-isotherm, TiO2, Interlayer distance.

Introduction

Hydrogen, a clean energy source that has been recently garnered attention as it does not pollute the air and is recycled into water after combustion, can be used and stored easily with a form of compressed or liquefied hydrogen. However, in order to store hydrogen with that form in the container, it must either meet high pressure conditions or be frozen to under -253 °C [1]. The hydrogen storage amount by this form in old physical storage technologies like these is dependent on the size and operating temperature of the container and also the injection pressure into the container, which have been known as inefficient, dangerous and with less cost-effective [2]. Recently, the utilization of nanotube and nano powders of carbon, sulfide and oxide based materials, and other porous materials with a high specific surface area for hydrogen storage has been suggested as alternative solutions to overcome the low energy efficiency, safety concern and economic problem of existing physical storage technologies and the problems associated with extremely low temperature and high pressure usages [3-6]. Unfortunately, these methods are also still problematic as the synthesis of the materials for hydrogen storage is very complicated and the adsorption between the surface or micro- or mesopores of materials and hydrogen molecules is also

unstable at room temperature and high temperature, resulting in fast desorption phenomena as the stored hydrogen escapes at the ambient conditions spontaneously [7-9]. This desorption also makes it difficult to understand the adsorption-desorption cyclic characteristics of materials and secure their reproducibility. Current technologies and those under development are unable to overcome the disadvantages posed by the extremely low temperatures needed to physically adsorb hydrogen molecules [10-13]. Accordingly, in order to utilize renewable hydrogen energy and at the same time to solve issues of the existing storage technologies and storage mediums, it will be necessary to develop a new form of efficient storage material that can store hydrogen molecules in ambient conditions.

In 1998, after Kasuga reported a synthesizing method of fibrous TiO₂ based nanotubes by hydrothermal synthesis in strong alkaline aqueous solutions, the TiO₂ based nanotube powder with high surface area using inexpensive synthesizing process has been widely studied as a promising new material for hydrogen storage [14-16]. The TiO_2 based nanotube powder by hydrothermal synthesis have been confirmed to have titanate crystallinity with a layered structure by the rearrangement of TiO₆ octahedra for forming fibrous $Na_xH_{1-x}O_yxH_2O$ nanotube (TiNT) powder in the strong alkaline aqueous solution. This is different from wellknown crystalline forms of TiO₂ such as anatase, rutile, and brookite [17-19]. Unlike the structure of existing porous materials, it was reported that hydrogen molecules might be stored even in the empty space between the tube walls as well as the conventional

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Sample Name	Sample Description	*H ₂ O Content (wt%)	Sodium Content (wt%)	Drying method, Temperature and time	Specific Surface Area (m ² /g)
AC	Activate Carbon	_	_	_	1153
ZSM 5x	Zeolite	_	_	_	400
M1	Ion exchanged titanate	31.5	0.03	Convection oven drying at 60, 24 hr	337
M2	Ion exchanged titanate	15.13	0.03	Freeze drying at -55, 48 hr	348
M2-1	Ion exchanged titanate	7.36	0.03	Freeze drying at -55, 48 hr, vacuum drying at 105, 2 4hr	344
M2-2	Ion exchanged titanate	4.81	0.03	Freeze drying at –55, 48 hr, Vacuum drying at 250, 24 hr	96
S0	Ion exchanged titanate with long time in 0.1N HCl aqueous solution	11.3	**ND	Freeze drying at –55, 48 hr, vacuum drying at 105, 24 hr	68
S 1	Ion exchanged titanate	5.82	8.36	Freeze drying at -55, 48 hr, vacuum drying at 105, 24 hr	240
S2	Ion exchanged titanate	6.21	4.27	Freeze drying at -55, 48 hr, vacuum drying at 105, 24 hr	275
S3	Ion exchanged titanate	6.29	2.48	Freeze drying at -55, 48 hr, vacuum drying at 105, 24 hr	301
S4	Ion exchanged titanate	6.73	1.36	Freeze drying at -55, 48 hr, vacuum drying at 105, 24 hr	324

Table 1. Physical properties of the powders.

*The H_2O content in all the powders was measured by using a moisture analyzer at 150 °C in the air environment and additionally was calibrated using the thermogravimetry.

**ND stands for not detected.

adsorption sites such as the particle surface and microor meso-pores in the titanate structure [20].

According to Lim et al.'s report as a first result for hydrogen storage using titanate, recently, the TiNT powder had a hydrogen storage capability of about 2 wt% at 59.2 atm at room temperature. Also, other researchers suggested that the TiNT material has good potential for promising hydrogen storage material operated even under ambient pressure and temperature since the primary problem for hydrogen storage materials of the state-of-the-art technologies is to use high pressure and temperature in the operating range [16]. However, because their hydrogen storage properties had been done on ion-exchanged proton-titanate (H-TiNT) powder, without detailed comments about Na⁺ and H₂O contents after preparation, their results could be very limited to synthesis reproducibility. Also, Kim et al. reported on the effects of heat treatment to increase the amount of storage in the TiNT of lithium ion with a decrease in moisture content in the secondary battery system [21]. Thus, it is necessary that intensive research should be carried out in details on the washing and drying methods for removing sodium element and water trapped in the powder from the synthesizing process with materials characterization for increase in hydrogen storage. Especially, in order to use the TiNT powder as a hydrogen storage material, the effect of H₂O content on the interior of the nanoparticles formed from hydrothermal synthesis must first be considered due to their interaction of hydroxide and the hydrogen

molecule. Second, the hydrogen storage characteristics caused by change of distance between the inter layers of nanotube made up of the multi-walls supported by sodium ion must also be examined. Therefore, the purpose of the present study is to evaluate the hydrogen storage properties with the quantitative controls of H_2O and sodium contents in the TiNT powder synthesized by hydrothermal synthesis.

Experimental

For the TiNT powder synthesis as reported previously, the starting material of 0.1 M P-25 TiO₂ powder (Degussa Co.) mixed with 10M NaOH aqueous solution was put into a stainless steel autoclave equipped with a nickel liner and then heated for a hydrothermal reaction at 150 °C for 48 hrs [22, 23]. After the reaction, precipitates with a high pH level from aqueous NaOH solution were washed repeatedly using distilled water to be maintained neutral, and then the obtained precipitate, as a intermediate product, having 8.36 wt% Na⁺ content at pH = 7.0 were again dispersed in 0.1 N HCI solution at 60 °C and agitated while the Na⁺ ions, trapped on the surface and interior of the particles during the hydrothermal reaction, were ion-exchanged with H⁺ and then became eliminated. During the ion-exchange processing, all the four samples with different Na⁺ contents were extracted. When measuring on the precipitates after drying, the Na⁺ contents of each precipitate were finally confirmed

To eliminate moisture or H₂O content from the obtained precipitates as much as possible, all five kinds of the samples were dried for 24 hrs using a freezedryer (ALPHA 1-2 LD, Christ). After the powders were freeze-dried they were again dried in a vacuum oven for 24 hours at 105 °C, dropping the moisture content amount down to $5 \sim 7$ wt%. For comparison, the powders with 0.03 wt% Na⁺ content was dried in an oven for 24 hrs especially in 60 °C and 250 °C, and then both of the powders had moisture amounts of 31.5 and 4.81 wt%, respectively. Here, the moisture in all the powders was measured by using a moisture analyzer (MX-30, AND) at 150 °C in the air environment and additionally was calibrated using the thermogravimetry (STA N-1500, Scinco). After all of the moisture of the dried powder was measured, the powders were kept in a moisture-controlled container to avoid their exposure to the ambient environment. The powders were then charged with the volume measurement based pressurecomposition(P-C)-isotherm unit (AnySorb HO, Mirae SI) for a hydrogen uptake or adsorption evaluation in the moisture-controlled condition. The degassing process in the P-C isotherm experiments was not adapted for additionally removing H₂O content in asdried powders.

The as-dried powders were observed to confirm a nanotublar shape by a scanning electron microscope (S-4700, Hitachi) and a transmission electron microscope (JEM-2010F, Jeol, Japan) and the Na⁺ ion content was analyzed with an EDX (Oxford INCA energy detector, equipped with SEM). The surface area of the powders was measured with BET (KICT-SPA3000, Mirae SI). The crystal structure was also measured by an X-ray diffractometer (D/MAX-2500/PC, Rigaku) and an ambient Raman spectroscopy (InVia Raman Macroscope, Renishow). The physical characteristics for all of the powders used and synthesized for this experiment are shown in Table 1.

Results and Discussion

SEM photographs for some samples with composition of Na_xH_{1-x}O_yzH₂O are representatively shown in Fig. 1 for confirmation of nano tubular shape gone through the ion-exchanging and drying processes. Together with the previous results summarized in Table 1, the titanates obtained by the hydrothermal synthesis have a high H₂O content of $15.13 \sim 31.5$ wt% even though their specific surface areas are more than 300 m²/g in case of suffering from simple processes of conventional oven drying and freeze-drying [24]. It was also observed that the specific surface area values of the other samples with Na⁺ ions more than 0.03 wt% were greatly increased with ion-exchanging with H⁺. It was observed that the powders (S1, S2, S3, and S4) with 8.36, 4.27, 2.48, and 1.36 wt% Na⁺ obtained with ionexchanging process, respectively, consist of the same nanotubular particles as that of M2-1 sample with 0.03 wt% Na⁺ obtained by sufficient ion-exchanging step, as seen in Fig. 1(a-b), including M1 and M2 samples. It is also found in Table 1 that the specific surface area value of the powders obtained under the same preparation conditions increased when the H₂O content decreased. However, if the ion-exchanging process was done for a long period of time for less than 0.03 wt\% Na^+ (S0 sample) or if the heat treatment was done at a high temperature of 250 °C (M2-2 sample), the nanotubular form of the particles was destroyed as shown in Fig. 1(c-d) and then their specific surface area values rather decreases greatly regardless of the drop in the H₂O content level. In summary, it can be thought that the titanate powders (TiNT) having a nanotubular form showed an increase in the specific surface area value with decreases in sodium content by the ion-exchanging process and in H₂O content by



Fig. 1. (a) SEM images of the powders M2-1, (b) TEM image of the powder M2-1, (c) SEM images of the powders M2-2 and (d) SEM images of the powders S0.



Fig. 2. Hydrogen uptake of the powders with various H_2O contents.

various drying processes and that they had not the nanotubular form when done by severe ion-exchanging and over-drying at high temperature.

Fig. 2 shows hydrogen uptake or adsorption characteristics measured with a P-C isotherm unit in the pressure range of ambient to 60 atm H₂ for the titanate samples having different H₂O contents with various drying processes summarized in Table 1. Here, the H₂O content was controlled for the samples (M1, M2, M2-1, M2-2 and S0 samples) with 0.03 or less wt% Na⁺ and then their characteristics were compared to that with 8.36 wt% Na⁺ (S1 sample) for very similar H₂O content in the M2-1 powders. In the S1 sample, hydrogen stores up to 1.56 wt% H₂ at 60 atm, showing an exponential hydrogen uptake characteristic with an increase in applied pressure. From the H₂ and N₂ desorption phenomena presented in Figs. 5 and 6, it can be said that its behavior corresponds typically to type 4 adsorption isotherm (IUPAC classification) having 2 stage adsorptions [25]. Namely, adsorption of hydrogen molecules in the TiNT particle is at first processed on the particle surface and between each particle, and then when the pressure increases the hydrogen adsorption increases inside by proliferation of nanopores or nanotube. As shown in Table 1, after the Na⁺ ion-exchanging process with the H⁺ ion, the specific surface area of the titanate powder has increased significantly and at the same time the H₂O content increased, but finally the amount of the hydrogen molecules adsorbed up to 60 atm becomes lower than the sample (S1) before the ion-exchanging process. Moreover, in the case of M1 sample, which contains 31.5 wt% H₂O, its uptake corresponding to the second adsorption stage does not show any progress compared with other powders and has only 0.63 wt% hydrogen adsorption content lower than the theoretical adsorption capacity (0.7 wt% H_2 at 337 m²/g and 60 atm, which can be gained when the adsorption capacity of the monolayer is assumed). This coincides with Kim et al.'s result that as the H₂O content decreases the adsorption amount of the hydrogen molecules increases for Ni-doped TiNT powder from the calcination in high temperature within a short time [26]. Therefore, it can be deduced that the ionexchange for Na⁺ elimination causes increases in the H₂O content as well as a specific surface area in the titanate powder and then that these behaviors ultimately disturb the adsorption of H₂ molecules to nanopores.

On the other hand, when the ion-exchanging process was done for a long period of time, the Na⁺ ion is almost completely removed as shown in S0 sample of Table 1. The adsorption behavior of S0 sample seems to be similar to that of the M2-2 sample, where the H₂O content is the lowest because it is heat-treated at 250 °C, showing a low specific surface area, and shows the smallest hydrogen molecule adsorption (0.18 wt%

Fig. 3. Raman spectroscopy results of the powders with various H₂O contents.

at 60 atm) due to a decrease in the amount of the adsorption site by shortening of the nanotube particles. Also, from the Raman spectra in Fig. 3, it can be observed that as the amount of Na⁺ content through ion-exchanging process decreases the crystalline structure of the titanate phase ("T" in the figure) gradually transforms into an anatase even without heattreatment. In other words, a TiNT powder (S1 sample) with 8.36 wt% Na⁺, gone through an ion-exchanging process, has a typical characteristic peak at 281 cm⁻¹, together with other peaks corresponding to perfect titanate phase. On the other hand, when compared to the powder (M2-2 sample) that had undergone heattreatment at 250 °C, the amount of the titanate phase obtained by the hydrothermal synthesis decreases with the ion-exchange, with developing the anatase phase ("A" in the figure) with the typical characteristics peaks at 145, 193, 401, 506 and 630 cm⁻¹ [24]. Thus, it can be thought that the elimination of the Na⁺ content from the particle by the ion-exchanging makes the nano tubular into rod typed particles consisting of the smaller-sized anatase phase, like the calcination effect at high temperature. From these results, it is inferred that this transformation of the titanate into the anatase phase caused to make hydrogen adsorptions difficult because the available space disappears. In conclusion, this result indicates that in order to enlarge the amount of the hydrogen adsorption on the titanate powders synthesized from the hydrothermal synthesis, not only the nanotubular form must be maintained but the Na⁺ content within the particle must also be controlled with lowering the H₂O content.

To improve the amount in the hydrogen uptake in a multi-walled TiNT particle, it will be naturally important to obtain the maximum surface site for the hydrogen

S ntensity(a.u M2 **S**0 M2-2 200 400 600 800 1000 Wave Number(cm⁻¹)





Fig. 4. Hydrogen uptake of the powders with various sodium contents.



Fig. 5. Hydrogen adsorption-isotherm results of the optimized powders with 2.41 wt% of Na⁺ ion and hydrogen uptake of commercial active carbon (AC) and zeolite (ZSM 5x).

molecule to spread toward each surface and interior or into the interspace between walls for its storage. According to Bavykin *et al.*, the interspace between the walls being consisted of TiNT can be controlled by existence of Na⁺ ion [18] and we had also reported the interspace became narrower with removing Na⁺ ions by increase in the ion-exchanging time [27]. Therefore, if the Na⁺ content can be adjusted while maintaining the constant H₂O content in the powder, the storage mechanism of hydrogen molecule with the form of TiNT particle can be understood, as can be seen in Fig. 4. Fig. 4 is the result of hydrogen adsorption in the TiNT powders containing different Na contents. As shown in the in-set figure, as the Na⁺ ion decreases, the amount of hydrogen adsorption gradually increases. When the powder had a 2.48 wt% Na⁺ ion, it shows the maximum amount in the hydrogen adsorption. When the Na^+ ion content decreases at less than 2.48 wt%, however, the amount of hydrogen adsorption also decreases. As the process of ion-exchanging takes places, the Na⁺ ions existing on surface of the particle and in its interior are eliminated and the specific surface area increases together, but when the Na⁺ ion is removed above any critical value, the titanate nanotube structure is destroyed and then the interval of each layer becomes narrower, interrupting the adsorption of the hydrogen molecule into the interspace between the walls. This indicates that the amount of hydrogen adsorption is lower at lower or higher Na⁺ contents because of it. It can be suggested that to make hydrogen adsorb and store easily, the appropriate concentration of the Na⁺ ion must exist to sustain the structure of the titanate nanotube.

Fig. 5 shows the result of hydrogen adsorption and desorption of the TiNT powder with the optimized content of 2.41 wt% Na⁺, compared with commercially available porous materials, Zeolite (ZSM 5x, Junsei Chemical Co.) and active carbon (AC, Junsei Chemical Co.). As seen in this figure, the active carbon with a specific surface area of 1500 m²/g and Zeolite with a specific surface area of 400 m²/g have only 0.75 wt% and 0.38 wt%, respectively, of hydrogen adsorption at 90 atm of H₂ applied because adsorption becomes saturated at more than about 40 atm although their absorptions increase with increasing applied pressure. No hysteresis curves observed with decreasing applied pressure due to the rapid release of adsorbed hydrogen. It is a typical Langmuir adsorption isotherm of type 1. On the other hand, the TiNT, which had a specific surface area of 300 m²/g, has about 2.21 wt% adsorption of the hydrogen molecule at 90 atm and a slow desorption processes because of adsorption filled the inside pore of tubular shape. It is worth noting that continuous adsorption of hydrogen with applied pressure indicates the TiNT material has still interlayer space for continuous uptake of hydrogen molecules. Nitrogen adsorption and desorption characteristics in the TiNT were tested using BJH and presented in Fig. 6. It shows that the TiNT powder has typical cylindrical BJH characteristics of pore in the range of $0.8 \sim 0.9$ of P/P₀ due to the tubular shape. This matched well with the ink-bottle theory [28]. Especially, in the desorption curves, the hydrogen molecules escape with delayed desorption under critical pressure differently from the hydrogen desorption of Fig. 5. This corresponds to the study of A. Mishara et al. whose results showed a hydrogen adsorption of anodized TiO₂ nanotube and delayed desorption being processed when the desorbed hydrogen separates as the pressure decreases. In case of other porous materials, they adsorbed the hydrogen from physisorption; however, as



Fig. 6. Nitrogen adsorption and desorption phenomena in the optimized powders with 2.41 wt% of Na⁺ using BJH method.

presented in Fig. 5, TiNT exhibits the hysterisis in the hydrogen adsorption curve. Defects in the TiNT such as voids or undangled sites in the interlayer space are responsible for the observed hysteresis. Due to the defects in the TiNT, the remained oxygen could be had a chance to bond with adsorbed hydrogen, and made an O-H bond in the TiNT. From this result, the TiNT showed the hysteresis in the desorption curves with decreasing applied pressure that means the mechanism of hydrogen adsorption in TiNT had both physical adsorption and chemisorption at applied pressure as reported by Lim *et al* [16].

On the other hand, according to Lim *et al.*'s report, the TiNT showed that the hydrogen adsorption was about 2.0 wt% at room temperature and at about 60 atm [16]. They also reported that the amount of the hydrogen adsorption consisted of about 75% of the physical adsorption, 13% of the weak chemisorption and 12% of the fusion between strong chemisorption was not observed as shown in Fig. 5. In conclusion, it can be clearly known that the hydrogen storage characteristics for the titanate nanotube powders was affected by H_2O content in the particle and their surface area adsorption sites including the multi-wall and the space between the interlayer of nanotubes.

Conclusions

Using alkali hydrothermal synthesis method, onedirectional structured titanate nanotube (TiNT) powders were synthesized and the hydrogen storage characteristics were evaluated. With removing of Na⁺ ions existed in the surface and the interior of particle by ion-exchange, titanate structure was collapsed, and then hydrogen uptake capability increased gradually and then decreased with changing into nano rod or spherical particle. Also, in order to control large amount of H2O contained in the TiNT powder, various drying methods were used and confirmed that the hydrogen uptake increased with decreasing H₂O content in the powder only under the condition of no particle shape change. Consequently, it is concluded that hydrogen molecules in the TiNT powders are at first adsorbed and filled into the empty spaces through particle surfaces, inter particle microand meso-pores, as the applied pressure increases. The powders with controlled H₂O and Na⁺ contents had high hydrogen uptake of 2.21 wt% at 90 atm due to proper support of Na⁺ for interlayer distance in multiwalled tube typed titanate particle. Therefore, to increase the hydrogen uptake in the titanate nanotube powder, it is necessary to maintain nanotubular shape and at the same time control the amount of H₂O existing on surface and interior sites of particles

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