

M. MATSUNAMI^{*,‡}, T. HASHIZUME^{**}, A. SAIKI^{**}ION-EXCHANGE REACTION OF A-SITE IN $A_2Ta_2O_6$ PYROCHLORE CRYSTAL STRUCTUREREAKCJA WYMIANY JONOWEJ W PODSIECI A W STRUKTURZE KRYSZALICZNEJ PIROCHLORU $A_2Ta_2O_6$

Na^+ or K^+ ion rechargeable battery is started to garner attention recently in Place of Li^+ ion cell. It is important that A-site ion can move in and out the positive-electrode materials. When $K_2Ta_2O_6$ powder had a pyrochlore structure was only dipped into NaOH aqueous solution at room temperature, $Na_2Ta_2O_6$ was obtained. $K_2Ta_2O_6$ was fabricated from a tantalum sheet by a hydrothermal synthesise with KOH aqueous solution. When $Na_2Ta_2O_6$ was dipped into KOH aqueous solution, $K_2Ta_2O_6$ was obtained again. If $KTaO_3$ had a perovskite structure was dipped, Ion-exchange was not observed by XRD. Because a lattice constant of pyrochlore structure of K-Ta-O system is bigger than perovskite, K^+ or Na^+ ion could shinnny through and exchange between Ta^{5+} and O^{2-} ion site in a pyrochlore structure. K^+ or Na^+ ion exchange of $A_2Ta_2O_6$ pyrochlore had reversibility. Therefore, $A_2Ta_2O_6$ had a pyrochlore structure can be expected such as Na^+ ion rechargeable battery element.

Keywords: $K_2Ta_2O_6$, $Na_2Ta_2O_6$, Ion-exchange, pyrochlore structure, perovskite structure

Akumulatory w którym jako nośniki ładunku wykorzystywane są jony Na^+ lub K^+ budzą coraz większe zainteresowanie jako alternatywa dla ogniw litowo-jonowych. Należy podkreślić, że kationy w podsięci A⁺ potrafią się przemieszczać z- i do dodatnio naładowanych materiałów elektrodowych. Gdy proszek $K_2Ta_2O_6$ posiadający strukturę pirochloru zanurzono w roztworze wodnym NaOH w temperaturze pokojowej, otrzymano $Na_2Ta_2O_6$. $K_2Ta_2O_6$ otrzymano poprzez obróbkę arkusza tantalu metodą hydrotermalną wykorzystując roztwór wodny KOH. Gdy zanurzono $Na_2Ta_2O_6$ w wodnym roztworze KOH, otrzymano z powrotem $K_2Ta_2O_6$. Natomiast, gdy zanurzono $KTaO_3$ o strukturze perowskitu, nie obserwowano wymiany jonowej. Dlatego, że stała sieciowa w strukturze pirochloru układu K-Ta-O jest większa niż w przypadku perowskitu, jony K^+ lub Na^+ mogą się poruszać i wymieniać w podsięci Ta^{5+} i O^{2-} w pirochlorze. Wymiana jonów K^+ lub Na^+ w pirochlorze $A_2Ta_2O_6$ jest odwracalna. Z tego powodu można się spodziewać, że związek $A_2Ta_2O_6$ o strukturze pirochloru może znaleźć potencjalne zastosowanie jako element akumulatora pracującego z jonami Na^+ .

1. Introduction

Li^+ -ion battery is rechargeable battery and charged and discharged by moving Li^+ -ion between the anode and the cathode. However, there is possibility that existence reserves of lithium is depleted by increasing the demand of lithium in recent years and anxiety that the supply amount of Li^+ -ion battery is limited in the future[1-4]. Thus, it is important that find alternative resources to lithium. Consequently, Na^+ -ion have been taken notice a substitute material for the Li^+ -ion.

In our laboratory, we found in the past study that $Na_2Ta_2O_6$ was obtained when $K_2Ta_2O_6$ powder had a pyrochlore structure was only dipped into NaOH aqueous solution at room temperature[15]. Thus, this had shown that Na^+ -ion was possible for the ion exchange required for cell reaction.

Therefore, in this study, these materials be looked these materials and the possibility as anode materials for batteries of Na^+ -ion be consider by studying the ion exchange of K^+ -ion or Na^+ -ion in detail.

2. Experimental

Firstly, $K_2Ta_2O_6$ was fabricated from a tantalum sheet by a hydrothermal synthesise with KOH (Kanto Chemical Co. INC., Cica-Reagent, 86.0%) aqueous (deionized water) solution[6-10]. The starting materials for the hydrothermal synthesis were Ta (Nilaco, 99.95%) and KOH. In a typical synthesis procedure, the Ta substrate(1.0×1.2 mm) and 4.0M KOH aqueous (1.5 ml) was poured into a Teflon container the autoclave with capacity of 2 ml. The autoclave was sealed and heated at 120°C for 2h. The resulting sample was washed with deionized water, then dried at room temperature. The sample was confirmed by X-ray diffraction (XRD on Shimadzu 6100 diffractometer) with Cu $K\alpha$ radiation ($\lambda = 1.5418\text{\AA}$). The XRD pattern was recorded from 10° to 80°(2 θ). $K_2Ta_2O_6$ was confirmed by XRD.

Next, $K_2Ta_2O_6$ was ion-exchanged by being dipped into NaOH (Kanto Chemical Co. INC., Cica-Reagent, 97.0%) aqueous at about 25°C. The sample was also confirmed by XRD under the same condition.

* GRADUATE SCHOOL OF SCIENCE AND ENGINEERING FOR EDUCATION, UNIVERSITY OF TOYAMA

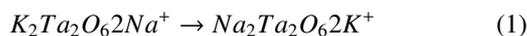
** GRADUATE SCHOOL OF SCIENCE AND ENGINEERING FOR RESEARCH, UNIVERSITY OF TOYAMA

‡ Corresponding author: m1471516@ems.u-toyama.ac.jp

3. Result and discussion

Fig. 1 showed XRD patterns of samples that $K_2Ta_2O_6$ before (a) and after (b)-(f) dipping into 6M-NaOH aqueous solution.

$K_2Ta_2O_6$ and $Na_2Ta_2O_6$ of the pyrochlore-type structure were confirmed in Fig. 1 (a) and (f). As a result, it was considered that ion exchange caused by equation:



when $K_2Ta_2O_6$ was only dipped into NaOH aqueous solution. The peak position of Fig. 1(b)-(e) was higher angle side than the peaks position of Fig. 1(a). It was considered that K^+ -ion and Na^+ -ion was sequentially replaced by ion exchange, and the peak of $K_2Ta_2O_6$ was reduced, the peak of $Na_2Ta_2O_6$ was increased.

Fig. 2 shows the lattice constant that calculated from the peak of (400) side of the XRD patterns in Fig. 1.

Consequently, it found that Na^+ -ion was changed and $Na_2Ta_2O_6$ could be again obtained by dipping into NaOH aqueous at room temperature.

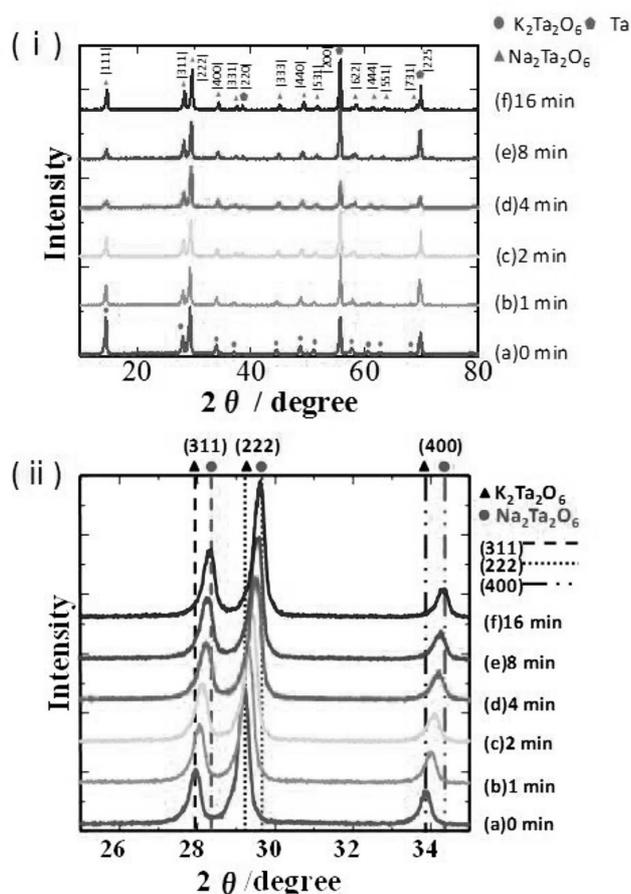


Fig. 1. (i) XRD patterns of the films ion exchange before (a) 0 min and after (b) 1 min (c) 2 min (d) 4 min (e) 8 min (f) 16 min in 6M-NaOH at 25°C, (ii) The enlarged patterns for the above ones at two theta ranging from 25° to 35°

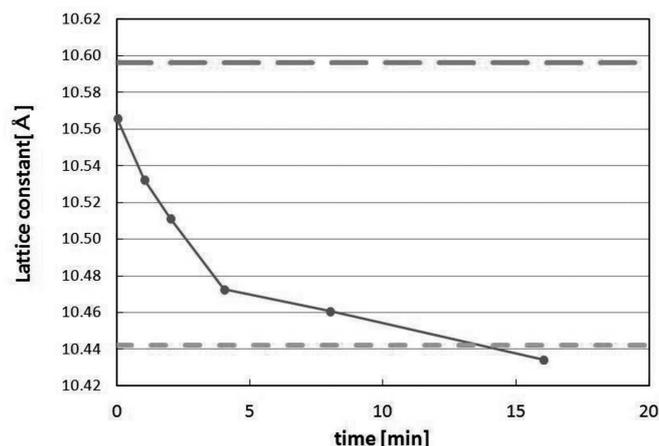


Fig. 2. Lattice constant of sample in 6M-NaOH

Fig. 3 showed the lattice constant calculated in the same way of Fig. 2 when $K_2Ta_2O_6$ dipped into (a) 1M (b) 2M (c) 4M (d) 6M-NaOH.

Ion exchange of reaction time was (a) 64 min (b) 64 min (c) 32 min (d) 16 min. As a result, reaction time of sample of Fig. 3(a) took longer than Fig. 3(d).

After ion exchange to $Na_2Ta_2O_6$, samples of Fig. 3(a)-(b) entered the saturation state, but samples of Fig. 3(c)-(d) still advanced reaction.

Consequently, it was considered that the ion exchange time taken longer because the concentration gradient in the reaction solution becomes small when reaction solution was a low concentration.

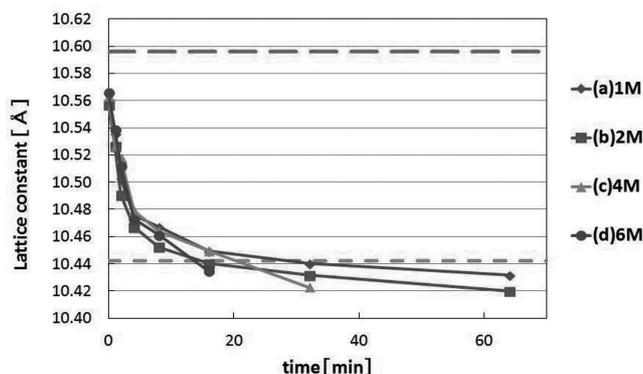


Fig. 3. Lattice constant of sample in (a) 1M (b) 2M (c) 4M (d) 6M-NaOH

Fig. 4 showed XRD patterns of samples when $K_2Ta_2O_6$ was dipped in 4M-NaOH \rightarrow 4M-KOH \rightarrow 4M-NaOH aqueous.

Fig. 4(a)-(b) and (e)-(j) showed that ion exchanged by $K_2Ta_2O_6$ was dipped in 4M-NaOH aqueous, and Fig. 4(b)-(e) show that $Na_2Ta_2O_6$ was dipped in 4M-KOH. $Na_2Ta_2O_6$ were confirmed in Fig. 4(b) and (j), and $K_2Ta_2O_6$ was confirmed in Fig. 4(e). It found that Na^+ -ion was discharged and $K_2Ta_2O_6$ could be again obtained by dipping $Na_2Ta_2O_6$ into KOH aqueous at room temperature.

Reaction time of ion exchange from $K_2Ta_2O_6$ to $Na_2Ta_2O_6$ took 32 min in the first reaction from Fig. 4(a)-(b), it took 16 min in the second reaction from Fig. 4(e)-(j). As a result, reaction time of the second was reduced to about 1/2 of the first. By ion exchanged once, it was considered that Na^+ -ion easily go in and out.

Consequently, the reversible ion exchange of K^+ -ion and Na^+ -ion was possible for $K_2Ta_2O_6$.

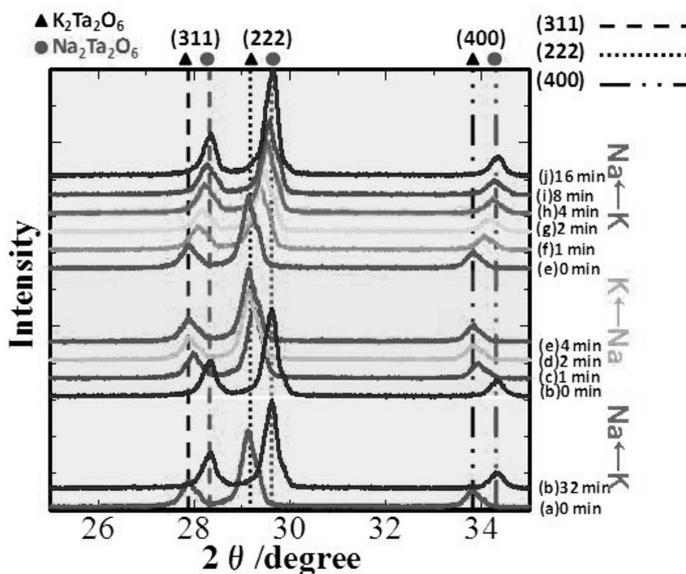


Fig. 4. XRD patterns of the films ion exchange before (a) 0 min and after (b) 32 min in 4M-NaOH, ion exchange (c) 1 min (d) 2 min (e) 4 min in 4M-KOH, next ion exchange (f) 1 min (g) 2 min (h) 4 min (i) 8 min (j) 16 min in KOH ($2\theta = 25^\circ$ to 35°)

$Na_2Ta_2O_6$ of the pyrochlore-type structure and $NaTaO_3$ of the perovskite-type structure was fabricated from a tantalum sheet by a hydrothermal synthesis with 4M-NaOH aqueous solution at $120^\circ C$ for 2h.

$Na_2Ta_2O_6$ and $NaTaO_3$ were ion-exchanged by being dipped into 4M-KOH aqueous solution at about $25^\circ C$.

As a result, when $Na_2Ta_2O_6$ was dipped into KOH aqueous solution, $K_2Ta_2O_6$ was obtained. However, when $NaTaO_3$ was dipped into KOH aqueous, $KTaO_3$ was not obtained. It was considered that the ion exchange depends on difference in crystal structure.

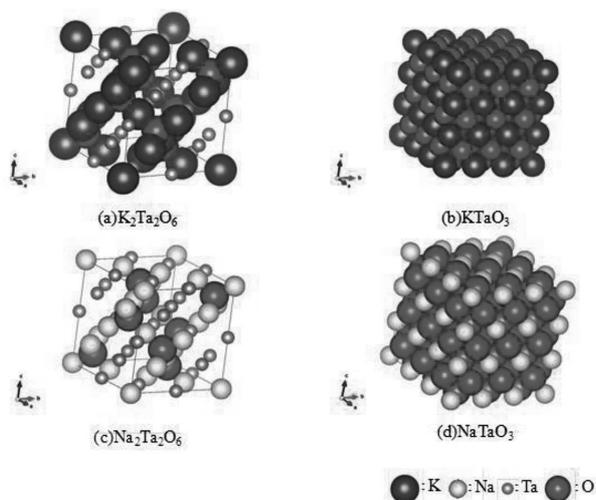


Fig. 5. Crystal structure of (a) $K_2Ta_2O_6$ (b) $KTaO_3$ (c) $Na_2Ta_2O_6$ (d) $NaTaO_3$

Fig. 5 showed crystal structure models of (a) $K_2Ta_2O_6$, (b) $KTaO_3$, (c) $Na_2Ta_2O_6$ and (d) $NaTaO_3$.

Comparing these crystal structure models, there were gaps that K^+ or Na^+ ion can go through between Ta^{5+} and O^{2-} ion site in the pyrochlore type structure. However, there was not the gap that K^+ or Na^+ ion can go through between Ta^{5+} and O^{2-} ion site in the perovskite type structure. Because atoms in the perovskite type structure are crowding.

Consequently, it found that the perovskite structure of A-Ta-O system does not occur ion exchange.

4. Conclusions

In summary, it looked like the following.

- $K_2Ta_2O_6$ was fabricated from a tantalum sheet by a hydrothermal synthesis with KOH aqueous solution. $Na_2Ta_2O_6$ was obtained by ion exchanged with Na^+ ion and K^+ ion in NaOH aqueous and $K_2Ta_2O_6$.
- $Na_2Ta_2O_6$ was fabricated possible by using NaOH aqueous of the low concentrations. K^+ or Na^+ ion exchange of $A_2Ta_2O_6$ pyrochlore had reversibility. In ion exchange from $K_2Ta_2O_6$ to $Na_2Ta_2O_6$, reaction time of the second was reduced to about 1/2 of the first.
- The perovskite structure of A-Ta-O system does not occur ion exchange.

Acknowledgements

This study was supported by Center for Instrumental Analysis, University of Toyama.

The authors would like to thank Mr. Yamada, Mrs. Hirata their experimental and technical supports.

REFERENCES

- [1] Weixin Song, Xiaobo Ji, Zhengping Wu, Yingchang Yang, Zhou Zhou, Fangqian Li, Qiyuan Chen, Craig E. Banks, Exploration of ion migration mechanism and diffusion capability for $Na_3V_2(PO_4)_2F_3$ cathode utilized in rechargeable sodium-ion batteries, *Journal of Power Sources* **256**, 258-263 (2014).
- [2] J.W. Liu, G. Chen, Z.H. Li, Z.G. Zhang, Hydrothermal synthesis and photocatalytic properties of $ATaO_3$ and $ANbO_3$ (A=Na and K), *Journal of Power Sources* **32**, 2269-2272 (2007).
- [3] Donghan Kim, Eungje Lee, Michael Slater, Wenquan Lu, Shawn Rood, Christopher S. Johnson, Layered $Na[Ni_{1/3}Fe_{1/3}Mn_{1/3}]O_2$ cathodes for Na-ion battery application, *Electrochemistry Communications* **18**, 66-69 (2012).
- [4] Damien Monti, Erlendur Jónsson, M. Rosa Palacín, Patrik Johansson, Ionic liquid based electrolytes for sodium-ion batteries: Na^+ salvation and ionic conductivity, *Journal of Power Sources* **245**, 630-636 (2014).
- [5] J.W. Liu, G. Chen, Z.H. Li, Z.G. Zhang, Hydrothermal synthesis and photocatalytic properties of $ATaO_3$ and $ANbO_3$ (A=Na and K), *International Journal of Hydrogen Energy* **32**, 2269-2272 (2007).
- [6] Matthew Mann, Summer Jackson, Joseph Kolis, Hydrothermal crystal growth of the potassium niobate and potassium tantalate family of crystals, *Journal of Solid State Chemistry* **183**, 2675-2680 (2010).
- [7] Koji Kajiyoshi, Kazumichi Yanagisawa, Masahiro Yoshimura, Hydrothermal and electrochemical growth of complex oxide thin films for electronic devices, *Journal of the European Ceramic Society* **26**, 605-611 (2006).

- [8] Shigeru Ikeda, Minoru Fubuki, Yoshiko K. Takahara, Michio Matsumura, Photocatalytic activity of hydrothermally synthesized tantalite pyrochlores for overall water splitting, *Applied Catalysis A: General* **300**, 186-190 (2006).
- [9] Gregory K.L. Goh, Sossina M. Haile, Carlos G. Levi, Fred F. Lange, Hydrothermal synthesis of perovskite and pyrochlore powders of potassium tantalite, *J. Mater. Res.* **17**, 12 (2002).
- [10] Tatsumi Ishihara, Nam Seok Baik, Naoko Ono, Hiroyasu Nishiguchi, Yusaku Takita, Effects of crystal structure on photolysis of H₂O on K-Ta mixed oxide, *Journal of Photochemistry and Photobiology A: Chemistry* **167**, 149-157 (2004).
- [11] Kevin S. Knight, Brendan J. Kennedy, Phase coexistence in NaTaO₃ at room temperature; a high resolution neutron powder diffraction study, *Solid State Sciences* **43**, 15-21 (2015).
- [12] Yoshio Waseda, Eiichiro Matsubara, Uchida Rokakuho co., Ltd., X-ray structure analysis-Determine the arrangements of atoms, Japan 1998.
- [13] Kento Sakuma, Sea sentence Temple publication co., Ltd., Ceramic materials, Japan 2007.
- [14] Manabu Seo, Mitsuo Abe, Takashi Suzuki, Kodansha, Ion Exchange-Advanced separation technology Foundation, Japan 1991.
- [15] Kazuyuki Hirao, Katsuhisa Tanaka, Atsushi Nakahira, Kinokuniya co., Ltd., Inorganic chemistry-the modern approach, Japan 2002.
- [16] Tomomi Sawai, Fabrication of multi-layered film of K(Na)-Ta-O thin film, Graduation thesis, University of Toyama, Toyama, Japan (2008).

Received: 20 February 2014.