

Master's Thesis

석사 학위논문

Studies on electrochemical magnesium intercalation in molybdenum trioxide

Hun-Ho Kwak (곽 헌 호 郭 軒 豪)

Department of Energy Systems Engineering

에너지시스템 전공

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By

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Department of Energy Systems Engineering

DGIST

A thesis submitted to the faculty of DGIST in partial fulfillment of the requirements for the degree of Master of Science in the Department of Energy Systems Engineering. The study was conducted in accordance with Code of Research Ethics¹

12. 05. 2013

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¹ Declaration of Ethical Conduct in Research: I, as a graduate student of DGIST, hereby declare that I have not committed any acts that may damage the credibility of my research. These include, but are not limited to: falsification, thesis written by someone else, distortion of research findings or plagiarism. I affirm that my thesis contains honest conclusions based on my own careful research under the guidance of my thesis advisor.

Studies on electrochemical magnesium intercalation in molybdenum trioxide

Hun-Ho Kwak

Accepted in partial fulfillment of the requirements for the degree of
Master of Science.

12. 05. 2013

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ABSTRACT

Electrochemical magnesium ion intercalation chemistry of MoO_3 has been studied in this work. Submicron-sized MoO_3 has been synthesized from commercial micron-sized MoO_3 by a facile oxalic acid method, which was confirmed by SEM and XRD. A beaker-type three-electrode measurement cell was designed using activated carbon as the counter electrode, which enabled the test of magnesium intercalation into the host material at the working electrode without problem when conventional organic electrolytes are used. The electrochemical magnesium intercalation into MoO_3 has been confirmed by cyclic voltammetry, galvanostatic discharge/charge, powder XRD and EDS measurements. Reversible reduction and oxidation peaks were observed in cyclic voltammograms as well as discharge/charge cycles, corresponding to magnesium insertion and deinsertion, respectively. The reversibility was also confirmed by XRD measurement which also showed that a new phase is formed during the discharge and the discharge/charge processes are

a pseudo two-phase reaction. With cycles, a degradation in crystallinity was observed.

Keywords : Submicron-sized MoO₃, beaker type three electrode measurement cell, activated carbon, pseudo two-phase reaction.

Contents

Abstract	i
List of contents	iii
List of figures	iv
1. Introduction	1
1.1 Principle of Magnesium battery	4
2. Experiments	5
2.1 Synthesis of submicron-sized MoO ₃	5
2.2 Preparation of electrodes and electrolyte, and materials characterization	5
2.3 Electrochemical cell configuration and characterization	6
3. Results and Discussion	9
3.1 Materials preparation	9
3.1.1 Synthesis of submicron-sized MoO ₃	9
3.2 Galvanostatic measurements	11
3.3 Structural change during first magnesium insertion process	14
3.4 Structural change during first magnesium de-insertion process	17
3.5 Cyclic voltammetry of Mg _x MoO ₃	20
4. Conclusions	22
References	24
요약문	25
Acknowledgement	27

List of Figures

Figure 1 Crystal structures of orthorhombic MoO ₃	2
Figure 2 MoO ₃ layer structure.	3
Figure 3 Scheme of reversible redox reaction of MoO ₃	3
Figure 4 Beaker-type cell configuration for electrochemical experiments.	6
Figure 5 Cyclovoltammogram to calibrate reference electrodes (Ag/Ag ⁺ (0.01 M AgNO ₃ and 0.25 M Mg(ClO ₄) ₂ in acetonitrile) tested with ferrocene in 0.25 M Mg(ClO ₄) ₂ solution	7
Figure 6 XRD patterns commercial MoO ₃ and after synthesis MoO ₃	9
Figure 7 SEM images of MoO ₃ particles : (a) Micron-sized particles of commercial (pristine) material; (b) Submicron-sized particles by thermal decomposition at 500°C for 4hr.	10
Figure 8 Scheme of discharge and charge of Experimental cell.	13
Figure 9 Discharge curve of MoO ₃ (cell's specific capacity is 186.715 mAh/g for ΔX=0.5).	14
Figure 10 During the magnesium insertion for Submicron MoO ₃	14
Figure 11 SEM image of discharged state of Mg _{0.5} MoO ₃	15
Figure 12 Charge curve of Mg _{0.5} MoO ₃	17
Figure 13 During the magnesium extraction for Submicron MoO ₃	18
Figure 14 EDS data for (a) MoO ₃ electrode (b) Mg _{0.5} MoO ₃	18
Figure 15 Cyclic voltammograms of Mg _x MoO ₃ in the electrolyte, 0.25 M Mg(ClO ₄) ₂ in acetonitrile Blue : 2 nd cycle, Red : 4 th cycle	20

1. Introduction

Researches on Mg-ion rechargeable batteries are still in its early stages. In the very near future, rechargeable batteries with high energy density, low cost and high safety will be highly needed. Lithium-ion batteries have some shortcomings related with safety problems, resource lack, and high cost. Future ESS, EV and portable devices requires more electrical energy. Recently researches on post-Li ion batteries have been receiving increasing attention to develop power sources based on natural abundant materials. We chose the "Magnesium" because, magnesium has green character, natural abundance, low equivalent weight, its low price and its safety characteristics. However, Mg batteries have not been studied much, because magnesium electrochemistry suffers from several serious limitations contrary to lithium electrochemistry: (i) difficulty in diffusion of the divalent Mg-ion in solid-state electrode compared to the monovalent Li-ion, (ii) the growth of an insulating passivation surface film on the Mg-metal anode that makes the electrodes useless electrochemically with the commonly used organic electrolytes, and (iii) the narrow electrochemical window of electrolytes for Mg-ion electrochemical activity [1]. These problems are what magnesium-ion battery researches have to overcome. There are several candidates proposed for positive electrode materials such as Chevrel phases $M_xMo_6T_8$ (M=metal, T=S,Se) [2], vanadium oxides [3,4], TiS_2 nanotubes [5] and graphite like

MoS₂ [6]. There are still some research activities in progress aiming to commercialize Mg-ion batteries. Orthorhombic molybdenum trioxide is known to be a typical host material for many monovalent and some multivalent cations that are inserted chemically or electrochemically [7]. In particular, MoO₃ is well known for reversible electrochemical insertion/de-insertion of lithium. And, this redox process is well understood. The intercalation of lithium in MoO₃ is derived from its special structure as shown

Fig.1.

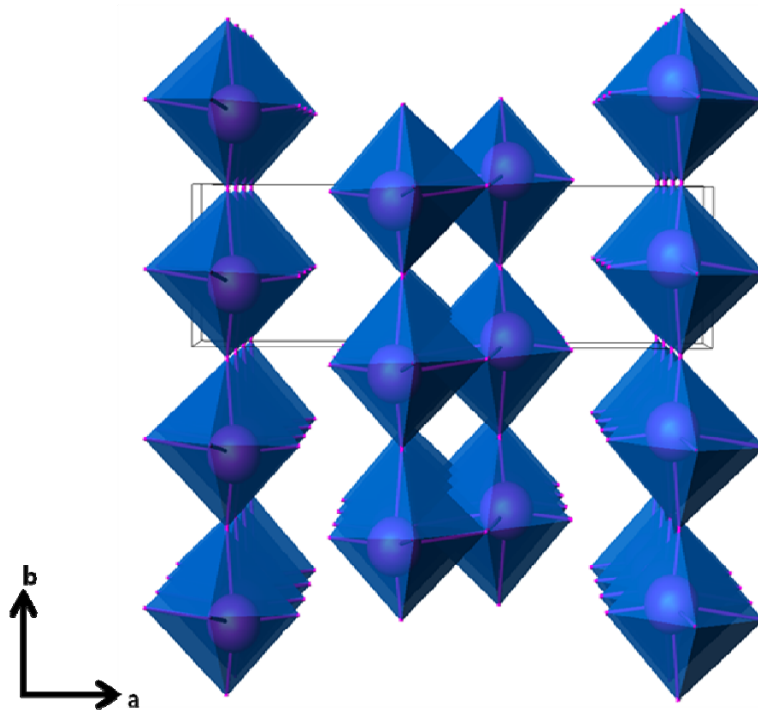


Figure.1 Crystal structure of orthorhombic MoO₃.

MoO₃ has an orthorhombic unit cell with the space group of *Pnma*, cell parameters $a=13.8674\text{\AA}$, $b=3.6976\text{\AA}$, $c=3.9644\text{\AA}$. [8] Mo-O octahedra form a double-sheets in the *bc*-plane. These sheets are stacked in *a*-direction with the van der Waals force between the layers as shown in Fig. 2. So, it al-

allows the reversible redox reactions, and the cations such as Li^+ , Na^+ , and Mg^{2+} could be intercalated into the interlayer space as shown in Fig.3. This work focuses on synthesis, establishment of cell configuration, and characterization of electrochemical insertion properties in non-aqueous electrolytes and structural changes during the intercalation of magnesium ions into MoO_3 host material. The ultimate aim of this study is to understand the complicated behavior of magnesium electrochemical intercalation into MoO_3 structure.

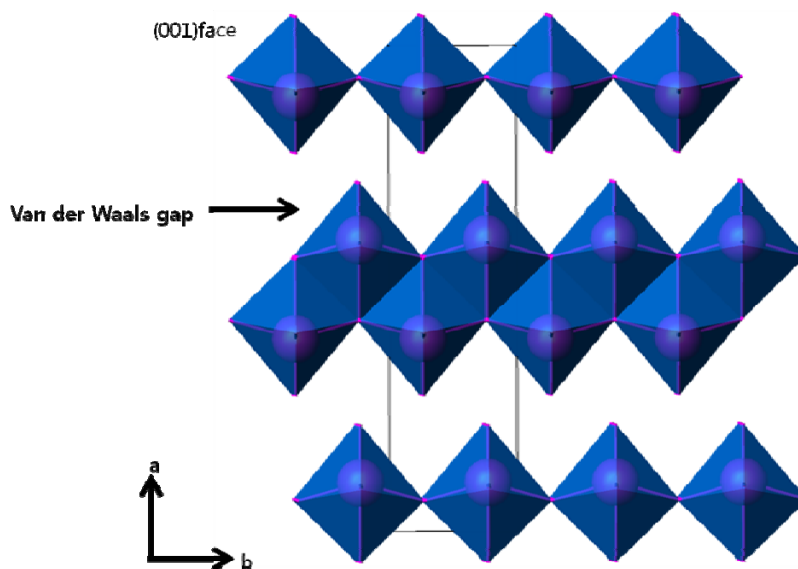


Figure.2 MoO_3 layer structure.

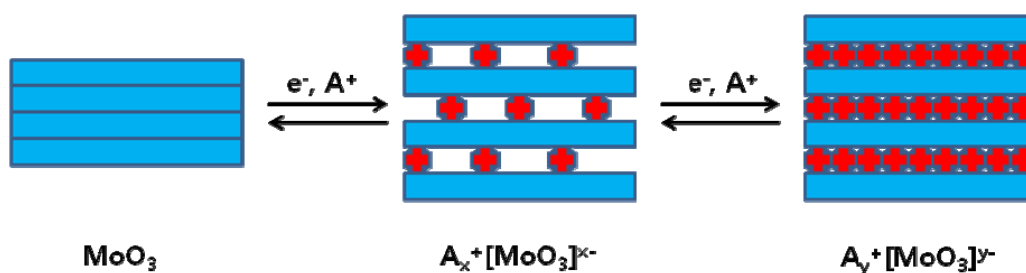


Figure.3 Scheme of reversible redox reaction of MoO_3

1.1 Principle of Magnesium battery

Mg batteries are based on the same principle as Li batteries, where the anode material and transport ion are magnesium metal foil and Mg^{2+} ions instead of Li metal foil and Li^+ , respectively.

Electrochemical magnesium deposition/dissolution reactions occur at the anode side, and intercalation reactions occur at the cathode side. For lithium battery case, the interphase between electrode and organic electrolytes is formed and it is called as solid electrolyte interphase (SEI) layer. This layer is electronically insulating but Li^+ ion conducting, and thus lithium can be used as an anode material in conventional organic electrolyte system. On the other hand, magnesium also forms a SEI layer in organic electrolyte system [9]. However, the layer is an insulator for both electrons and Mg^{2+} ions. That is the reason why the magnesium metal anodes can not be used as a reversible electrode material in conventional organic electrolyte systems. Since we cannot use magnesium metal as the anode in our experiments, we have designed an appropriate three-electrode measurement cell for the electrochemical characterization of magnesium ion intercalation into the host material as shown in section 2.3.

2. Experiments

2.1 Synthesis of submicron-sized MoO₃

There are various ways to improve electrode kinetics, such as decreasing particle sizes for the active materials, or modifying material morphologies as 1D nanorods, nanowires, and nanobelts. In this study, a facile synthesis technique was utilized to decrease the MoO₃ particle sizes [10]. Molybdenum trioxide (99.5%, Sigma Aldrich), oxalic acid (98%, Sigma Aldrich) were used. Micron-sized MoO₃ (4g) and oxalic acid (H₂C₂O₄) (15.01g) in a stoichiometric ratio of 1 : 6 were added to 200ml of distilled water and stirred at 80°C until they are dissolved completely. The solution was dried completely at 80°C for 5hrs, and further calcined at 500°C in air for 4hrs.

2.2 Preparation of electrodes and electrolyte, and materials

characterization

The electrolyte was prepared in glove box as 0.25M Mg(ClO₄)₂ (ACS reagent, Sigma Aldrich) in acetonitrile (99.8%, SAMCHUN CHEMICALS),. Because it was hard to completely remove the water content from Mg(ClO₄)₂ salt, the prepared solution of the fresh electrolytes contained quite a big amount of water, about 2000ppm. Thus, the water was to be removed from the electrolyte by a further drying

treatment using zeolite mesh (200mesh, Wako) and molecular sieve (3A, Yakuri), which are kept in the solution for more than a day. Then, the water content of the finally dried electrolytes were ~10ppm.

The XRD patterns of the materials and electrodes after electrochemical experiments were measured with a Bragg-Brentano type diffractometer (Miniflex 600, Rigaku) with $\text{CuK}\alpha$ radiation and graphite monochromator in a two-theta range between 5 to 70°, a step size of 0.02° and a duration time of 0.5 s. The materials morphology and elements analysis have been carried out with scanning electron microscope (SEM) and energy dispersive x-ray spectroscopy (EDS, S-4800, HITACHI).

2.3 Electrochemical cell configuration and characterization

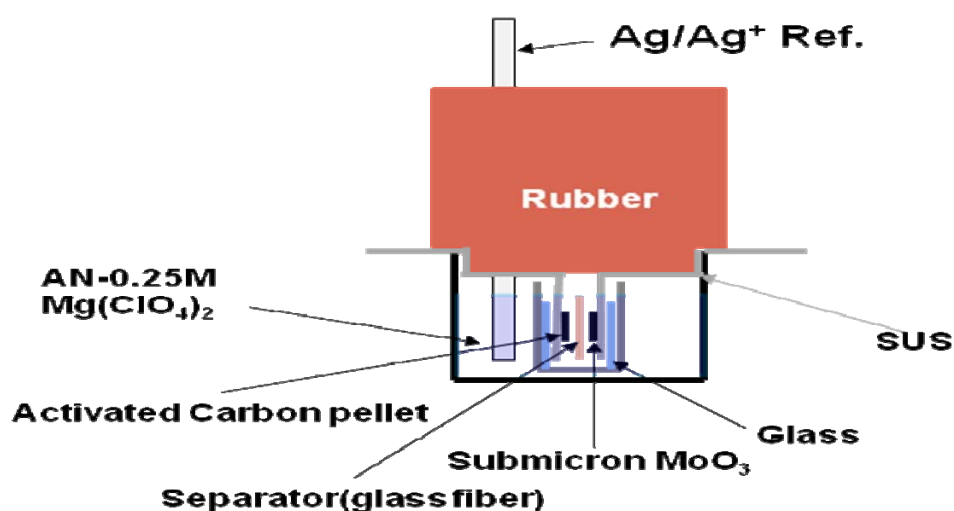


Figure.4 Beaker-type cell configuration for electrochemical experiments

Fig.4 shows the experimental beaker-type cell configuration for testing electrochemical properties of

MoO₃. The cells were assembled in a glove box with Ag/Ag⁺ (0.01 M AgNO₃ and 0.25 M Mg(ClO₄)₂ in acetonitrile) as the reference electrode, glass fiber as the separator and activated carbon pellet as the counter electrode. The reference electrode was calibrated by CV measurement with ferrocene solution as shown in Fig.5.

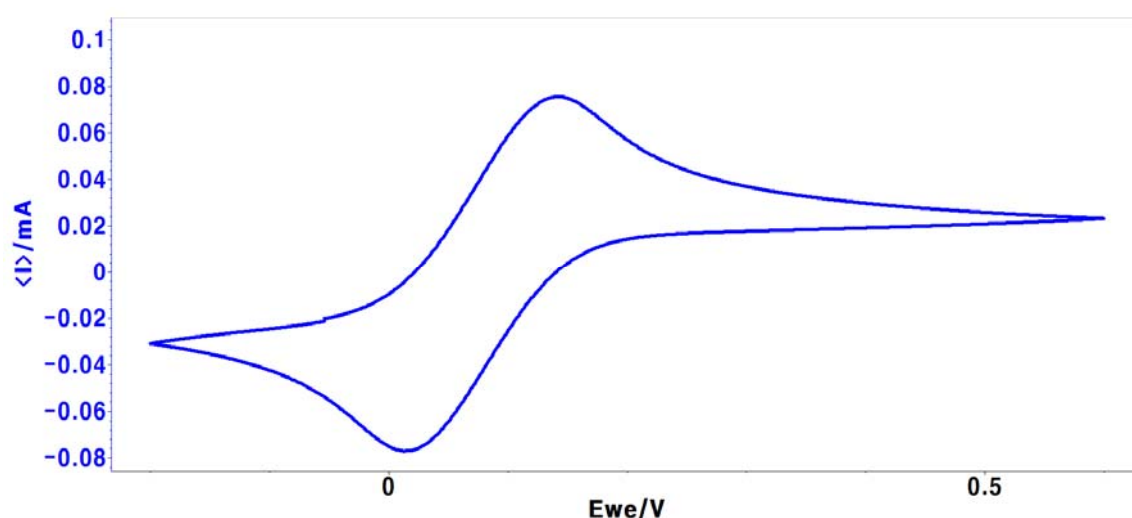


Figure.5 Cyclic voltammogram to calibrate reference electrodes (Ag/Ag⁺ (0.01 M AgNO₃ and 0.25 M Mg(ClO₄)₂ in acetonitrile) tested with ferrocene in 0.25 M Mg(ClO₄)₂ solution .

All the measurements were tested at room temperature and carried out in a glove box with less than 1 ppm of water and oxygen-content. A slurry mixture of MoO₃ (active material) , carbon black (SuperP, Timcal) and PVdF (binder, KF1100) in a weight of 8 : 1 : 1 was well mixed using a THINKY mixer (Thinky). The primer (Henkel, Dag EB-012) was used to enhance adhesion between stainless steel with active materials. Then, the working electrodes were prepared by coating the mixture on primer

coated stainless steel foils of 10 μ m thickness, using a Mini coater (Hohsen), followed by drying at 80°C and pressing (Wellcos Corporation). The electrodes have a thickness of 35 μ m, a loading density of ~0.39mAh/cm², and porosity of ~68%. The counter electrodes were prepared in a form of pellets using a die, which were mixtures of activated carbon (Daejung Chemicals & Metals) and poly(tetrafluoroethylene) (Sigma Aldrich) in a weight of 7 : 3.

3. Results and Discussion

3.1 Materials preparation

3.1.1 Synthesis of submicron sized MoO₃

The method used in this work is a low cost and template free method to synthesize submicron-sized particles by thermal decomposition. In order to confirm the phases, the diffraction patterns for micron-sized (pristine) and submicron-sized (synthesized) MoO₃ are compared in Fig.6. The reflection peaks are broadened for the submicron-sized MoO₃, indicating smaller crystallite particle sizes than the raw material, which is consistent with the SEM images shown in Fig.7.

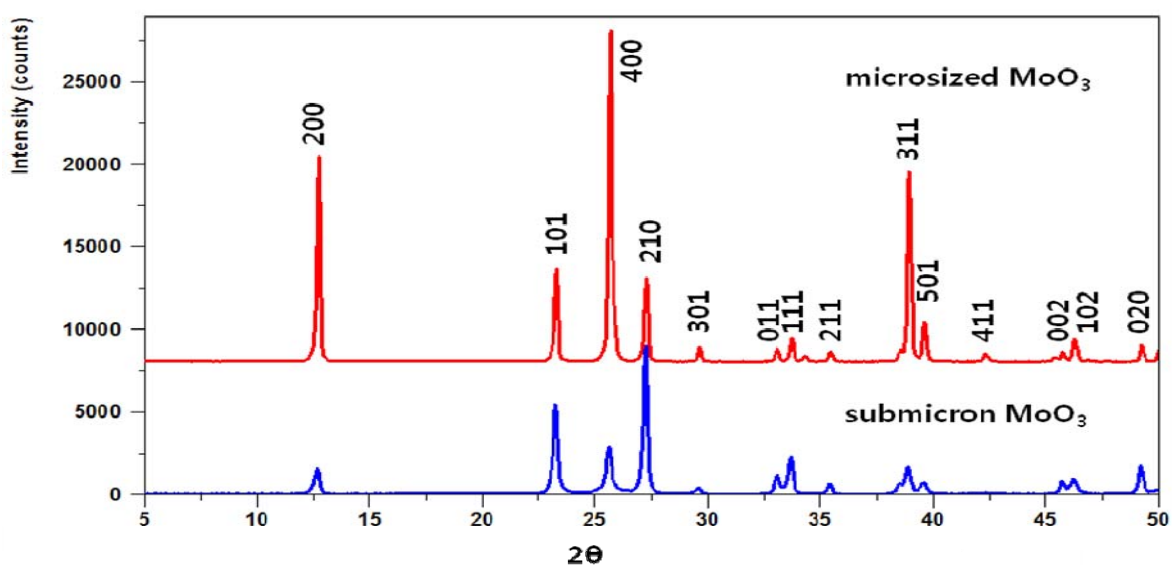


Figure.6 XRD patterns commercial MoO₃ and after synthesis MoO₃

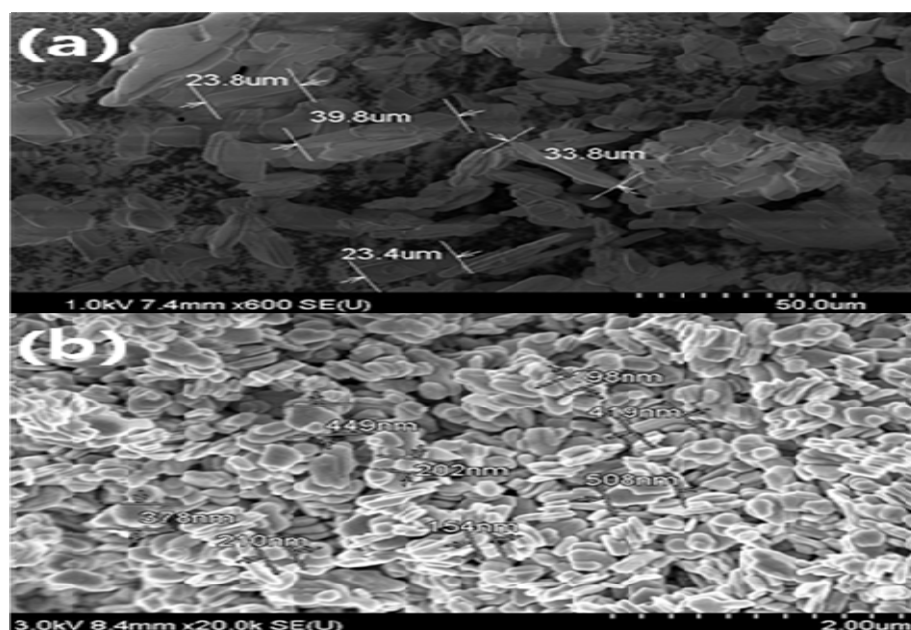


Figure.7 SEM images of MoO_3 particles : (a) Micron-sized particles of commercial (pristine)

material; (b) Submicron-sized particles by thermal decomposition at 500°C for 4hr

The SEM images of MoO_3 particles show clearly the difference of the particles sizes. The particle sizes of the commercial (pristine) MoO_3 are micron-sized with $20\sim 40\ \mu\text{m}$ (Fig.7a). For the synthesized MoO_3 by thermal decomposition at 500°C for 4hr (Fig.7b), the particles become submicron-sized with $200\sim 500\text{nm}$, which are much smaller (about $1/100$) than the starting material of MoO_3 .

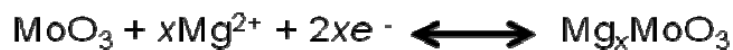
3.2 Galvanostatic measurements

In our test cells, the activated carbon pellet used for the counter electrode could be one of the most important key roles for making the electrochemical intercalation test enabled. The designed electrochemical test cell is a hybrid cell of capacitor and battery. Ion adsorption and desorption reactions occur at the activated carbon electrode, which is the principle for a capacitor. On the other hand, an intercalation reaction occurs at the MoO_3 working electrode, which is the principle for a typical metal ion battery. In the electrolyte, magnesium perchlorate is dissociated into Mg^{2+} and $(\text{ClO}_4)^-$ ions. Thus, when the discharge (reduction) starts, Mg^{2+} ions are inserted into the layer of the MoO_3 structure. At the same time, $(\text{ClO}_4)^-$ ions are adsorbed on the activated carbon surface. In the case of charge, the reverse reaction occurs. The activated carbon, just enabling adsorption and desorption reactions, does not form any passivation barrier. There is no passivation problem that is observed on Mg metal surface with a conventional organic electrolyte. Thus, such a cell configuration enables us to test the electrochemical Mg^{2+} insertion/de-insertion reactions into the positive electrode materials. Otherwise, even the test itself was not possible. Fig.8 shows the scheme of the mechanism of the experimental cells during discharge and charge.

MoO_3 is known for a poor electrochemical stability. In Li-ion battery case, during the first lithiation,

MoO₃ reaches almost the theoretical value of the specific charge of 300-350 Ah/kg, which enters into a significantly fading in subsequent cycles [11]. This problem is ascribed to the low conductivity for both electrons and cations, and the rearrangement of molybdenum and oxygen atoms during the first insertion [12]. Considering such a property of MoO₃, the experiments were performed with low C-rates. When the cell was tested with C/20 rate or little faster rate, the potential of cell was dropped (or elevated) very fast, thus leading to the lower (or upper) cut-off voltage, due to a severe overpotential. Discharge or charge test with slow rate (C/200 rate) was necessary to make the overpotential low enough to perform the experiments within a tolerable voltage window less than 2V range. It is obvious that the slowly tested cells (C/200 rate) reach equilibrium at each stage of the discharge/charge, so as to make the structural and electrochemical analyses more reliable.

The Mg²⁺ intercalation reaction into MoO₃ can be described as follows :



In the following section, we will discuss about XRD patterns related with discharge and charge curves.

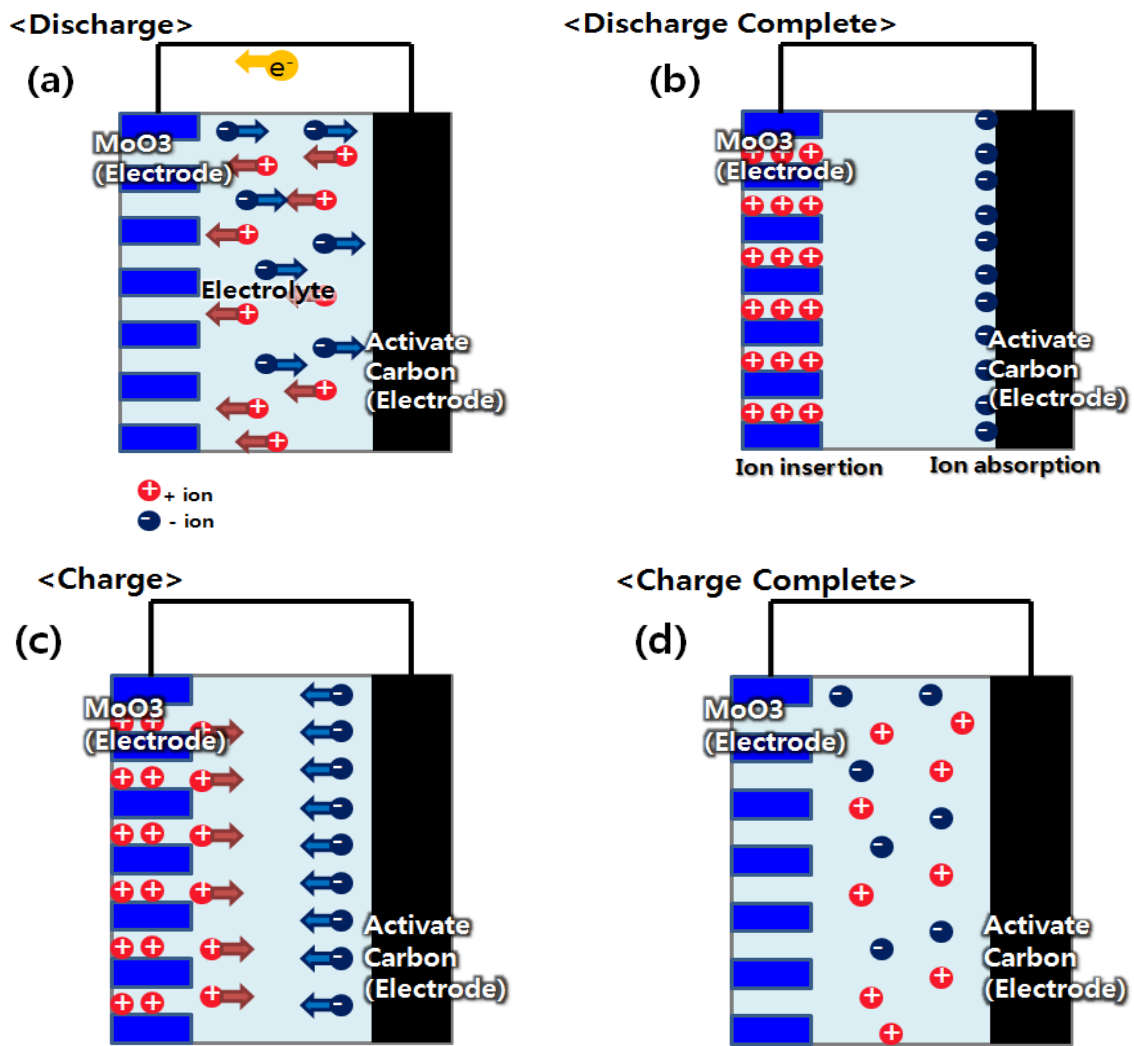


Figure.8 Scheme of discharge and charge of Experimental cell

3.3 Structural change during first magnesium insertion process

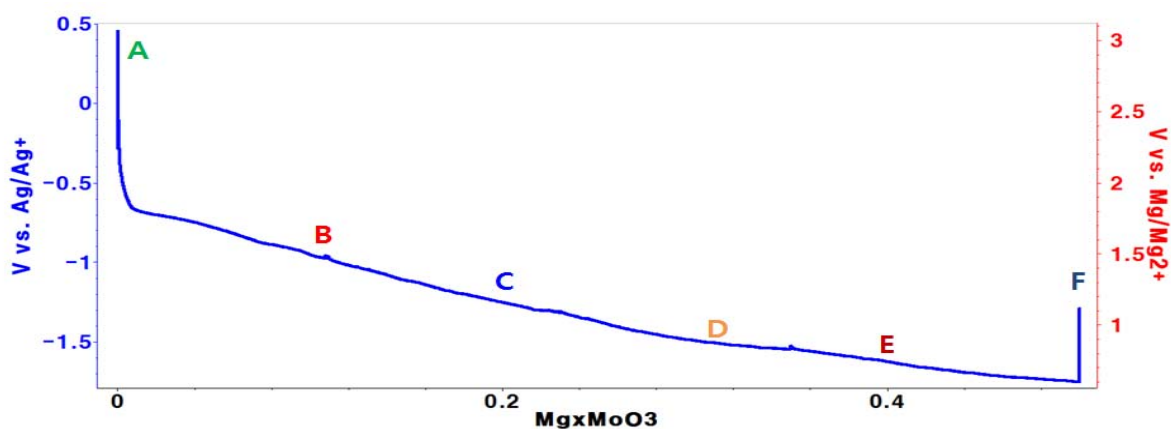


Figure.9 Discharge curve of MoO₃(cell's specific capacity is 186.715 mAh/g for $\Delta X=0.5$)

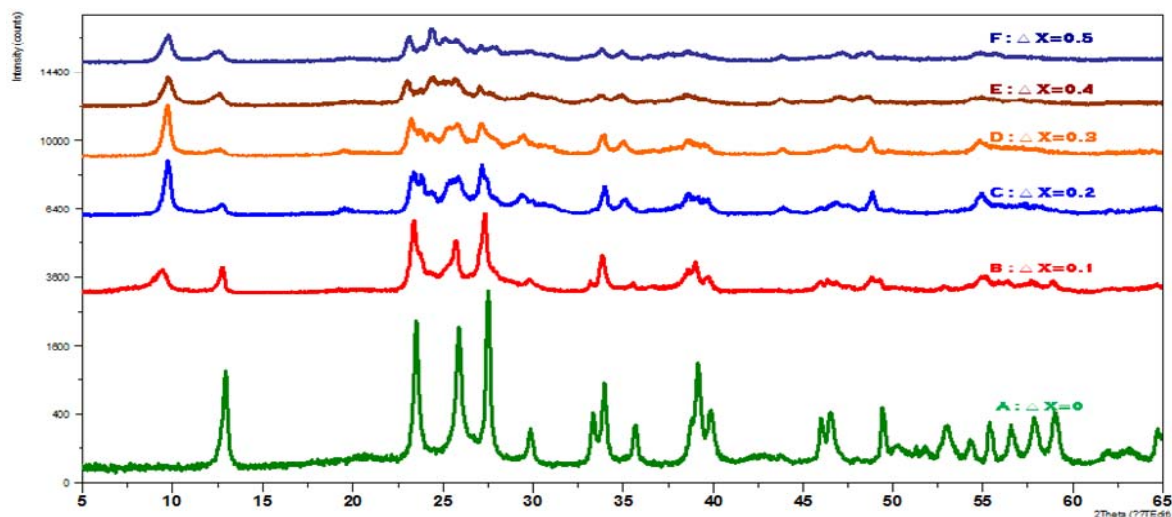


Figure.10 During the magnesium insertion for Submicron MoO₃

The discharge curves of Mg_xMoO₃ and the corresponding changes in XRD patterns during magnesium insertion are shown in Fig.9 and Fig.10, respectively. The XRD patterns from A to F in Fig.10 refer to the corresponding points on the discharge curve in Fig.9. The discharge curve shows a linear and gentle slope, indicating that the magnesium insertion reaction into MoO₃ could be a single phase re-

action. It is, however, obvious that at least a new phase appeared immediately when MoO_3 is discharged (or reduced), but a smaller amount of the original phase still remains in the XRD pattern, though the amount seems to be more reduced with discharge. Thus, the reaction may be a pseudo two-phase reaction, and the sloping curve could be due to decreased electronic conductivity of Mg_xMoO_3 with higher x content, resulting in increased overpotential during the discharge. A dramatic and immediate change in the XRD patterns with discharge is a strong evidence indicating the possibility of Mg^{2+} ions insertion into the bulk host material of MoO_3 , not surface reaction or electrolyte decomposition reaction. As the more magnesium ions are inserted to MoO_3 , the pristine MoO_3 gradually disappears and a new phase grows up. Pristine MoO_3 almost disappears around the $\text{Mg}_{0.5}\text{MoO}_3$. The complicated XRD pattern for the new phase means MoO_3 structure is distorted a lot as Mg^{2+} ions are inserted.

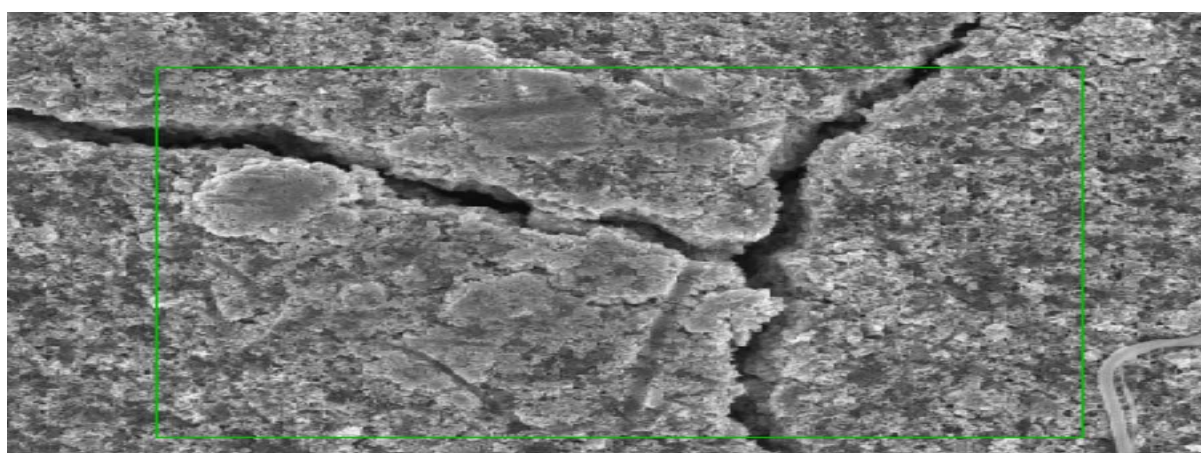


Figure.11 SEM image of discharged state of $\text{Mg}_{0.5}\text{MoO}_3$

Fig.11 shows a SEM image for the discharged state of $Mg_{0.5}MoO_3$. A lot of cracks are seen in the electrode. MoO_3 is known to suffer from slow kinetics and volume change [11]. The cracks seem to be a consequence of a large volume change during magnesium insertion, which is consistent with the dramatic change in structure. The loss of electronic paths due to the cracks may also be responsible for the linearly sloping discharge curve for the two-phase reaction that is supposed to show a flat curve.

3.4 Structural change during magnesium de-insertion process

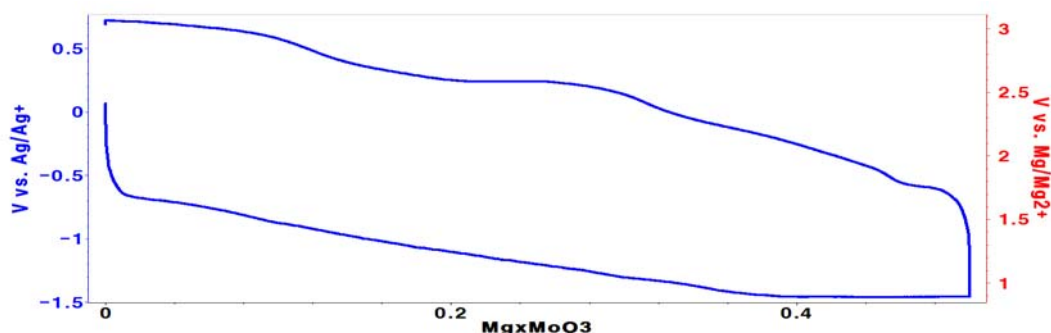


Figure.12 Charge curve of $\text{Mg}_{0.5}\text{MoO}_3$

In order to see the reversibility of magnesium insertion/de-insertion reaction, a series of experiments have been done as follows: a sample was first discharged to a state at $\Delta X=0.1$ ($=\text{Mg}_{0.1}\text{MoO}_3$), and then it is returned to a state at $\Delta X=0$ ($=\text{MoO}_3$) by charging. In this way, several samples were prepared with different depth of discharge (DOD) ($\Delta X=0.2$, $\Delta X=0.3$, $\Delta X=0.4$, $\Delta X=0.5$), followed by being charged to the original state of $\Delta X=0$. For example, one cycle of discharge ($\Delta X=0.5$, or $\text{Mg}_{0.5}\text{MoO}_3$) followed by charge ($\Delta X=0$ or $\text{Mg}_0\text{MoO}_3=\text{MoO}_3$) is shown in Fig.12, for which the specific capacity corresponds to 187 mAh/g. The XRD patterns for the returned phases that had experienced different DOD. values before charging are shown in Fig.13. It is clear to see that the XRD patterns for the returned phases are almost the same as the pristine MoO_3 , suggesting that magnesium intercalation into MoO_3 is reversible. It was also observed that the crystallinity became worse according to the broader reflection peaks for the returned phases. The higher DOD. a sample experiences, the more

degradation in crystallinity it shows. In other words, the more deformation in crystal structure a sample experiences, the less it keeps the original phase. According to this fact, it is anticipated that MoO_3 would experience a strong capacity fading with cycles, as observed in Li intercalation case.

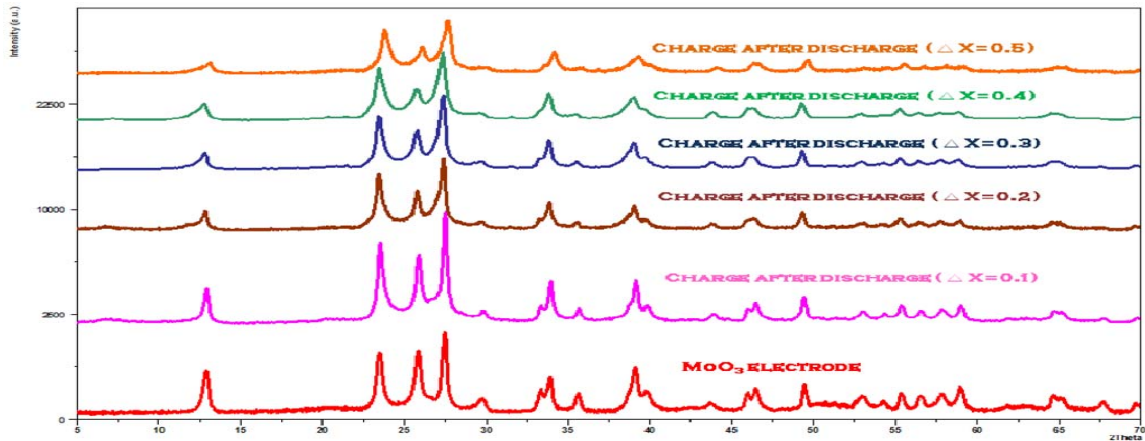


Figure.13 During the magnesium extraction for Submicron MoO_3

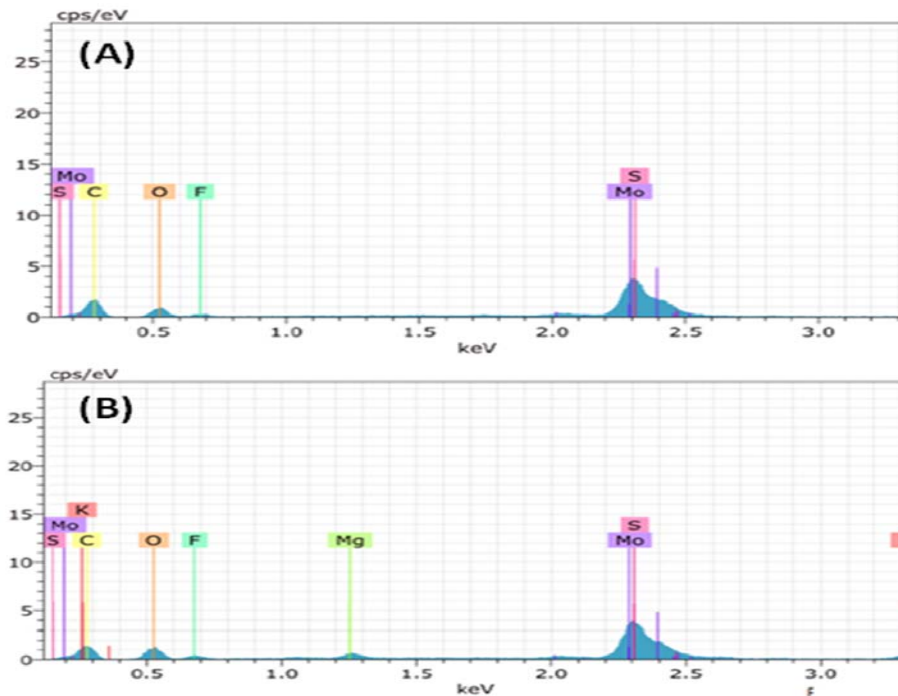


Figure.14 EDS data for (a) MoO_3 electrode (b) $\text{Mg}_{0.5}\text{MoO}_3$

Fig.14. shows a comparison of Energy Dispersive x-ray Spectroscopy (EDS) results for (a) a fresh MoO_3 electrode, and (b) the $\text{Mg}_{0.5}\text{MoO}_3$, respectively. Magnesium was observed for the sample of $\text{Mg}_{0.5}\text{MoO}_3$, not for MoO_3 , as expected. It is to be noted that the EDS samples were washed carefully and thoroughly, so that no electrolyte remained before the measurement. Even though the EDS data reflect the surface state, the results seem to be a reliable evidence that magnesium ions are intercalated to MoO_3 .

3.5 Cyclic voltammetry of Mg_xMoO_3

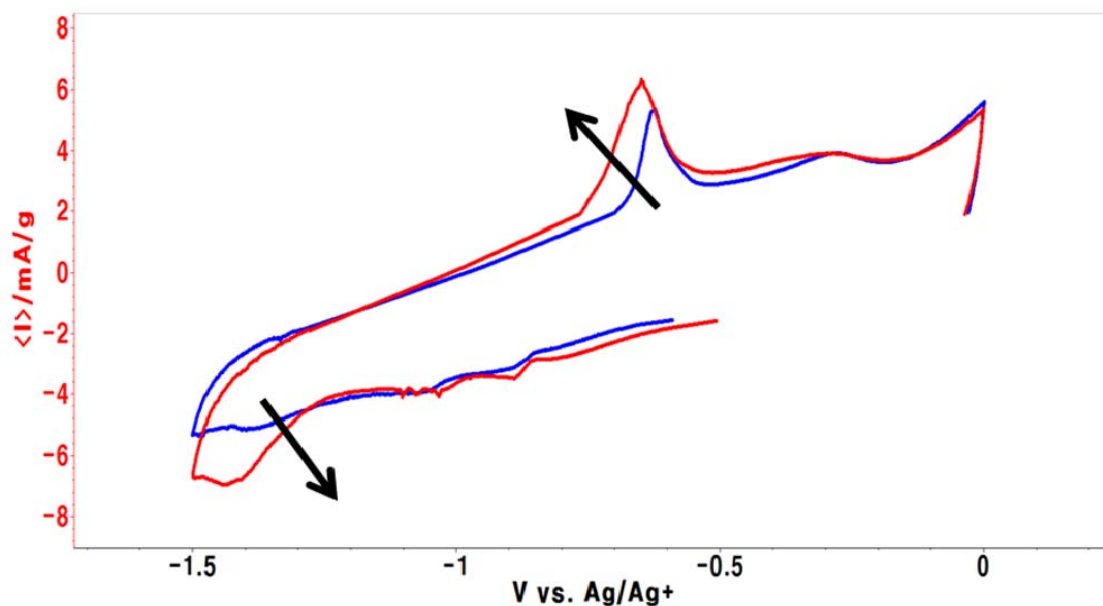


Figure.15 Cyclic voltammograms of Mg_xMoO_3 in the electrolyte, 0.25 M $\text{Mg}(\text{ClO}_4)_2$ in acetonitrile

Blue : 2nd cycle, Red : 4th cycle

The cyclic voltammograms were measured with a scan rate 0.02mV/s from 0 V to -1.5 V versus Ag/Ag⁺. Fig.15. shows CVs for the 2nd and the 4th cycles. In this CVs, reduction and oxidation peaks correspond to magnesium insertion and deinsertion, respectively. Reversible insertion/de-insertion peaks are observed, also indicating that the Mg^{2+} intercalation into MoO_3 is reversible, consistent with previous results reported in reference [14], where the intercalation/deintercalation of Mg^{2+} ions between MoO_6 octahedron interlayers are described. For a first few cycles, the peak intensity

increases, as if MoO_3 structure gets activated. That is, the sepecific capacity may increase somehow for a few cycles, but the crystallinity becomes worse with more cycles.

4. Conclusions

Electrochemical magnesium ion intercalation chemistry of MoO_3 has been studied in this work. Submicron-sized MoO_3 has been synthesized by a facile oxalic acid method. With SEM and XRD the formation of the submicron-sized MoO_3 was confirmed. Since magnesium metal cannot be used as an anode material in electrochemical experiments using conventional organic electrolytes, we have designed an appropriate measurement cell for test. MoO_3 was used as a working electrode for magnesium intercalation host, and activated carbon pellet was used as a counter electrode. The magnesium intercalation in MoO_3 and its electrochemical properties have been characterized, by cyclic voltammetry, galvanostatic discharge/charge, and powder XRD measurements. Reduction and oxidation peaks were observed at cyclic voltammograms which correspond to magnesium insertion and deinsertion, respectively. The Mg^{2+} insertion/deinsertion reaction into MoO_3 was turned out to be reversible with a pseudo two-phase reaction during discharge and charge processes. With cycles, a degradation in crystallinity was observed.

In this work, we have clearly demonstrated that Mg^{2+} can be electrochemically intercalated into MoO_3 host material. It seems, however, that magnesium ion batteries still are a long way to replace the lithium ion batteries in terms of energy density and power. But, we could see a possibility of mag-

nesium ion batteries. Further studies should be focused on discovering new host materials with high energy density. The magnesium batteries will surely be promising for energy storage systems in near future.

요약문

MoO₃에 관한 마그네슘이온 전기화학적 탈/삽입 연구

MoO₃를 working electrode로 사용하여, 마그네슘 이온 전기화학적 탈/삽입 연구를 진행하였다.

Oxalic acid 합성 방법을 이용하여, Submicron-sized의 MoO₃를 합성하였고, SEM과 XRD로

확인하였다. 실험은 beaker type-cell, three electrode cell test을 진행하였으며, reference electrode로

Ag/Ag⁺, counter electrode로 activate carbon을 사용하였다. Activate carbon을 이용함으로써, 기존

유기전해액에서는 실험이 불가능했던, host 물질에 대한 magnesium intercalation 실험을

가능케하였다. MoO₃에 magnesium intercalation은 cyclic voltammetry, galvanostic dis-

charge/charge, powder XRD, EDS로 측정 및 분석을 하였다. Cyclic voltammograms에서 가역적인

환원, 산화 피크가 관찰되었으며, 충방전 실험 또한, magnesium insertion과 deinsertion이 확인

되었다. XRD 분석결과, 충방전 과정에서 MoO₃는 two-phase reaction을 갖는다는 것을 확인

하였고, 충방전이 진행됨에 따라, 결정성이 나빠진다는 것을 관찰할 수 있었다.

핵심어 : Submicron-sized MoO₃, beaker type three electrode measurement cell, activated carbon,

pseudo two-phase reaction.

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바보는 천재를 이기지 못 하고,
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