

論文 / 著書情報
Article / Book Information

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(博士課程)
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論文要旨

THESIS SUMMARY

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Department of		
学生氏名:	李 蔚	
Student's Name		

申請学位(専攻分野):	博士	(工学)
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Academic Advisor(sub)		

要旨 (英文 800 語程度)
Thesis Summary (approx.800 English Words)

Introduction: Lithium ion batteries (LIBs) have been considered to be the most advanced means of energy storage in the near future. The charge/discharge time is becoming increasingly important in evaluating the performance of LIBs for their use in electric vehicles and other applications. Internal resistance is a key factor determining the high-rate charge/discharge performance of electrodes. Although much effort has been made to study Li ion transportation to increase the charge/discharge rate, there has been little research on electron conduction to our knowledge. Hence, in this work, the study on electron resistance and reaction resistance from the viewpoint of electron conduction in the electrodes will be focused. Tungsten trioxide (WO_3) crystalline thin film was chosen for the electrodes in this study. To improve the charge/discharge rate, it is necessary to increase the electron conductivity of crystalline WO_3 thin films. In this study, improvement of electron conductivity of WO_3 and its effect on improvement of charge/discharge performance of LIBs was investigated.

Results and Discussions: Electron conductivity property of monoclinic WO_3 (m- WO_3) thin film was studied by measuring resistivity through the four-point probe method. Annealing in N_2 reduces the resistivity of the m- WO_3 film, subsequent annealing in 5% O_2 +95% N_2 ambient results in the resistivity returning to its initial value. The changes in the resistivity after annealing in N_2 or 5% O_2 +95% N_2 ambient can be explained by oxygen vacancy generation and annihilation in a WO_3 thin film. Activation energy (E_a) values were approximately 0.2 eV, indicating that oxygen vacancies stably exist at approximately 0.2 eV below the bottom of the conduction band. For the samples annealed at temperatures from 300 °C to 500 °C, the gradients of the curves were almost the same as that for the sample without annealing. On the other hand, for the samples annealed at temperatures from 600 °C to 750 °C, the curves could be divided into two parts with different gradients. The first part is in the temperature range from 443 K to 393 K, which has almost the same gradient as that for the sample without annealing. The other part is in the temperature range from 373 K to 243 K, which has a smaller gradient. This can be explained by resistivity fitting of the 700 °C-annealed and 750 °C-annealed samples using a mixture of band conduction and nearest-neighboring hopping (NNH) conduction. It is suggested that two conduction mechanisms simultaneously exist in the electron conduction of m- WO_3 thin films. Moreover, after high-temperature annealing in N_2 , the NNH conduction mechanism becomes dominant owing to the increased number of oxygen vacancies. Then we used the WO_3 electrode as the positive electrode with Li metal as the negative electrode to investigate the charge/discharge characteristics. It was demonstrated that the electron conduction of electrodes greatly impacts the charge/discharge performance of LIBs by

evaluating the performance of LIBs with WO_3 electrodes having different conductivities. The potential difference between the anodic peak and cathodic peak of cyclic voltammetry curves decreased as the annealing temperature increased revealing the improved reversibility of the electrode reaction. Cole–Cole plots showed that electrode-reaction resistance decreased as annealing temperature of the electrodes increased. To verify the increase in the charge/discharge rate discussed above, the charge capacities were measured at charge rates of 0.2, 1, and 5 C. As the charge rate increased, the capacity of the sample with the electrode not subjected to annealing decreased by the largest amount, and the sample with the 700 °C-annealed electrode showed the best performance. The XRD patterns revealed that annealing at 300 °C in N_2 ambient did not change the monoclinic crystalline structure, whereas annealing at 700 °C in N_2 ambient changed the monoclinic structure into a cubiclike structure, which was reported to promote Li ion intercalation owing to its all 90° bond-angles.

Conclusions: Electron Conduction of WO_3 : 1) Electron conduction property of WO_3 powder thin films was improved by N_2 annealing. Higher temperature showed lower resistivity. 2) N_2 annealing induced oxygen vacancies which stably exist at approximately 0.2 eV below the bottom of the conduction band. 3) Two conduction mechanisms simultaneously exist in the electron conduction of m- WO_3 thin films. After high-temperature annealing in N_2 , the NNH conduction mechanism becomes dominant owing to the increased number of oxygen vacancies. **Performance of LIBs with WO_3 electrodes:** 1) Increasing the electron conductivity of WO_3 electrodes can markedly improve the charge/discharge rate and reversibility. 2) Oxygen vacancies may cause crystalline structure to change into cubiclike structure, which may promote Li ion intercalation. 3) Crystalline WO_3 was demonstrated to be a promising material for electrodes since oxygen vacancy generation can be induced by a simple annealing treatment, improving the electron conduction and Li ion transportation.

備考：論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1 copy of 800 Words (English).

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