

論文 / 著書情報
Article / Book Information

題目(和文)	
Title(English)	In-situ electron microscope study on a LiMn2O4 Li-ion battery cathode
著者(和文)	LeeSoyeon
Author(English)	Soyeon Lee
出典(和文)	学位:博士(理学), 学位授与機関:東京工業大学, 報告番号:甲第9414号, 授与年月日:2014年3月26日, 学位の種別:課程博士, 審査員:山本 直紀,菅野 了次,平山 博之,佐々木 聡,川路 均
Citation(English)	Degree:Doctor (Science), Conferring organization: Tokyo Institute of Technology, Report number:甲第9414号, Conferred date:2014/3/26, Degree Type:Course doctor, Examiner:,,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

(博士課程)
Doctoral Program

論文要旨

THESIS SUMMARY

専攻 : Department of	材料物理	専攻	申請学位 (専攻分野) : Academic Degree Requested	博士 (理学) Doctor of (理学)
学籍番号 : Student ID Number			指導教員 (主) : Academic Advisor(main)	山本 直紀
学生氏名 : Student's Name	LEE SOYEON		指導教員 (副) : Academic Advisor(sub)	佐々木 聡

要旨 (英文 800 語程度)

Thesis Summary (approx.800 English Words)

In-situ transmission electron microscope (TEM) observation of a LiMn_2O_4 nanowire battery was performed for revealing the mechanism of capacity fade out during 4 V charge/discharge reaction. LiMn_2O_4 crystal is a promising cathode material for lithium ion batteries (LIBs) because of the high natural abundance of manganese.

This thesis consists of six chapters. In chapter 1, the structure of LIBs and the aging phenomena which is important issue for long life time of LIBs are introduced. To improve the life time, the aging mechanism, irreversible local structure change, is required to be understood. Therefore, real-time observation during charge-discharge cycles was performed by TEM.

In chapter 2, as a new microscope method to image lithium ion behavior in LIBs, annular bright field (ABF) imaging was investigated. We demonstrated that lithium atoms in the diffusion channel of the spinel structure (a thin LiV_2O_4 crystal) were visualized and their number was countable one-by-one by using ABF imaging method: the lithium column intensity varied with increasing number of single lithium atoms in correlation with the thickness change of the LiV_2O_4 crystal.

A through-focus series of ABF images of a thin LiMn_2O_4 crystal were observed in order to clarify the image mechanism. Contrast reversal of an atomic column depending on the defocus reversal proved the ABF imaging to be a potential imaging of individual atomic columns.

The proportional relationship of the ABF image contrast to the number of ions has enabled us to study motion of ions through the contrast change accompanied with structure change. During the structural transformation of spinel LiV_2O_4 crystals into defective $\text{Li}_x\text{V}_2\text{O}_4$, ABF images revealed that lithium ions displacement from the tetrahedral sites induced the redistribution of vanadium ions at octahedral sites. *In-situ* ABF imaging of thin specimens is a promising method for investigating local structural transformations accompanied by lithium movement.

The ABF image taken with a large convergence angle is sensitive to the top surface and is useful to image the surface profile of LIB electrode materials such as vacancy or adsorption.

From the chapter 3, we focused on the structure change of a LiMn_2O_4 cathode material during the battery cycles. In chapter 3, the development of a “nano-battery” using LiMn_2O_4 nanowires is introduced. The LiMn_2O_4 nanowires were suspended on ionic liquid electrolyte placed upon $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode. The nano-battery was observed to work as a 4V rechargeable battery, showing clear current peaks in the cyclic voltammetry.

In chapter 4, during charge and discharge cycles, structure change was observed by *in-situ* TEM with simultaneous electrochemical measurement which was cyclic voltammetry. The LiMn_2O_4 nanowire cathode was found to be changed partially into the tetragonal phase (Li excess state) at the interface region adjacent to the electrolyte during the discharge process of the 4 V reaction (vs Li/Li^+). The lithium ions were inserted into the nanowire at higher rate than diffused to the bulk-side of the nanowire. The tetragonal phase of the LiMn_2O_4 cathode was restored to be cubic phase without any fracture in the charge process. No fracture while cubic-tetragonal transition is promising for the long-life-time battery with LiMn_2O_4 nanowire cathode.

In chapter 5, we developed a single nanowire battery for investigating lithium diffusion behavior in the bulk-side of LiMn_2O_4 nanowire. During a discharge-charge process, the phase boundary between Li-poor and Li-rich cubic structures was probed. The phase boundary advanced toward Li-poor phase during discharge process, indicating the volume of Li-poor phase decreased. The phase boundary movement reversed during charge process. However, the phase boundary was observed to move even after cathodic/anodic current stopped. It indicated that lithium ions diffusion was not limited by the phase transformation. The charge capacity estimated from the phase boundary movement was about 30 times smaller than the one estimated from the simultaneously obtained CV curve. The phase transformation is considered to occur at multiple positions along the nanowire simultaneously and to be completed with the time delay due to redistribution of lithium ions inside the nanowire after charge/discharge process.

In this study, the phase transformation of a LiMn_2O_4 crystal during charge/discharge process was observed at the bulk-side of LiMn_2O_4 nanowire and at the interface region between LiMn_2O_4 and the electrolyte. Lithium diffusion inside LiMn_2O_4 nanowire was not limited by the phase transformation between Li-poor and Li-rich phases. However, the lithium insertion rate from the electrolyte into LiMn_2O_4 was still higher than the rate of lithium diffusion from the interface region to bulk-side of the LiMn_2O_4 nanowire.

This study suggests that the 1-dimensional morphology is the most profit for a LiMn_2O_4 cathode material. It prevents the capacity fade out due to the severe volume change of LiMn_2O_4 crystals during the transformation between tetragonal and cubic phases. For the case of common batteries where whole body of a LiMn_2O_4 crystal is soaked in electrolyte the 1-dimensional morphology allow whole body of the nanowire to be regarded as interface region with electrolyte. It would enable fast charge/discharge process.

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 2 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 2 copies of