# 論文 / 著書情報
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# 論 文 要 旨

THESIS SUMMARY

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| 学籍番号：<br>Student ID Number | | 指導教員（主）：<br>Academic Advisor(main) | 准教授 脇慶子 |
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要旨（英文 800 語程度）
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**In chapter 1 (Introduction)**, a brief explanation on the carbon nanotubes and the application for electrochemical energy storage devices, particularly Li secondary batteries has been conveyed. In this chapter, the explanation is started from the concept of Lithium of batteries, including the current electrode materials available in the market. Later, background of carbon nanotubes, together with different defect preparation was explained, in order to give the reader a strong foundation on "what is the defective carbon nanotubes." Review of carbon nanotubes application for anode and recent cathode material for Li ion battery application then described. Finally, the research goal of current study was proposed

**In chapter 2 (Defects fabrication on multiwalled carbon nanotubes: characterizations and application for LIB anode materials)**, a study on defective multiwalled carbon nanotubes (DMWCNTs) and their application of Li storage anode material was explained. Defective multiwalled carbon nanotubes have been prepared by using cobalt oxide as the solid-state catalyst. It was shown from the thermogravimetric analysis study, that using such catalyst, the oxidation temperature of CNTs can be decreased up to 250 $^{o}$C. The resulting DMWCNTs were characterized by different tools, to clarify the defect formation. Increasing the $I_D/I_G$, together with TEM images, has proved the presence of defects. DMWCNTs then were applied as the Li storage anode material. It was found that compared to the purified and pristine MWCNTs, DMWCNTs showed the largest storage capacity of 625 $mAhg^{-1}$. By using the defective structures, not only high performance of anode material can be achieved, but also provide us a better understanding on Li storage mechanism. Here, we hinted that extraction at the high potential may not be related to the extraction of Li bound surface groups, as evidenced by the estimated Li storage capacity derived from evaluating the amount of functional groups. The author proposed that such extraction might come from the extraction of Li from in-plane defects.

**In chapter 3 (What is actually extracted at high potential? Revealing the relationship between functional group and Li storage sites for CNT based anode materials)**, we focus the study on clarifying what actually extracted at high potential. As many groups have reported, such extraction is related to the extraction from Li bonded surface functionalities. However, in the contrary, our previous result (chapter 2) suggested that the functional groups may not relate to such characteristics. Realizing that the our proposed model in chapter 2 was built based on o-containing functional groups. Thus, in this chapter, a systematic study was conducted by studying the MWCNTs with and without functionalities for Li storage materials. Considering that slurry casted electrode contain binder, and may interrupt our characterization on MWCNTs. We prepared our home-made, free-standing MWCNT electrodes, by simple vacuum filtration. The use of the MWCNT paper electrode offers the possibility to study the sole characteristic of CNTs. Following to our goal in this chapter, the functional groups on MWCNTs were eliminated by annealing under Ar atmosphere for 1 hour, at 900 $^{o}$C. Meanwhile, thermal desorption analysis was utilized to evaluate the functional groups on MWCNTs before and after annealing. It has been confirmed that such

annealing has removed the functional groups from the surface. Interestingly, eventhough after annealing, pristine, purified and DMWCNTs contain a comparable amount of functional groups. However, the Li storage capacities are different each other. By correlating the functional group content and capacity derivation study, we can confirm for the first time, that functional groups likely not related to the Li extraction at high potential. We then proposed two scenarios of trapping sites for explaining the Li extraction at high potential on oxidized MWCNTs, first the in-plane defects and secondly, solid electrolyte interphase (SEI) itself as trapping site. Preventing the carbon anode with minimum SEI formation and study their storage capacities are the key to clarify the role of SEI for trapping the Li ions.

**In chapter 4 (Defective multiwalled carbon nanotubes: a study for cathode application)**, We attempts to use the functional groups on the oxidized MWCNTs as cathode materials. As suggested from our previous findings (chapter 2 and 3), functional groups likely will not give any effect on Li storage for anode material. Benefiting from the Faradaic reaction between functional groups and Li ions, the purified and DMWCNTs were applied for studying such possible application. In order to study the role of surface functionalities, MWCNTs were annealed at 500 and 900 $^{o}$C to selectively remove the carboxyl and all functional groups, respectively. Thermal desorption analysis was conducted to monitor the type and quantity of O-functionalities, during the annealing processes. It is important to note that, after annealing at 500 $^{o}$C, the previous observed redox reaction peaks on the as prepared MWCNTs have disappeared. This suggests that the Faradaic reaction may be exclusively come from the reaction between carboxyl group and Li. Hence, modifying the CNTs with more fraction of carboxyl group than the carbonyl one becomes an important key to reach high performance carbon-based cathode materials for Li ion battery application.

**In chapter 5 (Conclusions and prospective studies)**, In this chapter, we conclude our story while giving some hints for the future works that need to be done.