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（博士課程）
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論 文 要 旨

THESIS SUMMARY

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学生氏名： Student's Name	Hansen Chang	指導教員（主）： Academic Advisor(main)	Prof. Ryoji Kanno
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要旨（和文 2000 字程度）
Thesis Summary（approx.2000 Japanese Characters ）

In this study we attempted to synthesize $Li_{1+x}[Li_{0.2}Mn_{\alpha}Co_{\beta}Ni_{\gamma}]O_2$ where $x > 0.0$ using a high pressure method. Initial experiments used a stoichiometric composition of starting materials to achieve precise molar ratios of compositions. A trend towards a cubic phase was found as x increased with a simultaneous decrease in Li. Inactivity of Li_2O during high-pressure synthesis was blamed. The next composition only used Li_2O_2. Results revealed Li rich samples with capacities near 200 mAh g^{-1}. Extra oxygen from the Li2O2 is assumed to have evaporated during synthesis. Oxygen rich synthesis was further explored with excess oxygen conditions with an KClO4 oxygen generator. Changes in transition metal valences were observed and capacities above 200 mAh g^{-1} were achieved.

In order to develop practical all electric vehicles a battery with a higher capacity and safer operation is necessary. The new material with Li excess and a ternary transition metal system composed of Mn, Co and Ni is promising, but not yet fully mature. In order to find the direction of research needed in order to for these types of materials to become practical it is necessary to investigate the origin of the over-capacity. In this study we attempted to synthesize the Li-rich phase which is thought to appear after the initial charge and oxygen generation plateau. To create this phase, which is more lithium rich, and can be expressed as $Li_{1.2+x}M_{0.8}O_2$, a high-pressure synthesis method was used. This method has the benefit of directly controlling the synthesis stoichiometry in a sealed environment, and it is thought the high-pressure condition will facilitate the insertion of Li into the layered structure beyond that of $Li_{1.2+x}M_{0.8}O_2$. Creating a new Li rich material should help solve the mechanism of the over-capacity, and open up potentially new types of materials that have yet not been studied.

In this study, stoichiometric $Li_{1+x}[Li_{0.2}Mn_{\alpha}Co_{\beta}Ni_{\gamma}O_2$, where $0.0 \le x \le 0.6$, was synthesized using a high-pressure method using Li_2O and Li_2O_2 in the starting precursor. The transition metal ratio was either $\alpha = 0.3$, $\beta = 0.2$ and $\gamma = 0.3$ or $\alpha = 0.2$, $\beta = 0.2$ and $\gamma = 0.4$. X-ray diffraction measurements were performed, and the structure was identified as *R*-3*m,* a Li_2O impurity was also found. Furthermore a trend towards a more cubic structure was identified as x increased and the Li_2O impurity increased as x increased. To remove the impurity the materials were washed in ethanol and then filtered and dried. Inductively coupled spectroscopy (ICP) revealed that after the ethanol wash, a Li poor composition was obtained. Neutron diffraction measurements also revealed a *R*-3*m* structure that was Li poor. It was surmised that

Li_2O inactivity was the probable culprit. Electrochemical charge-discharge experiments revealed that a capacity of around 200 mAh g^{-1} were still achieved despite no evidence of a Li excess structure being found. The plateau, which is associated with the oxygen generation, diminished as *x* increased.

To avoid the Li_2O impurity and increase Li content, $Li_{1+x}[Li_{0.2}Mn_{0.2}Co_{0.2}Ni_{0.4}]O_2$ was synthesized using a high-pressure method but this time the starting precursor contained only Li_2O_2. The effective starting precursor composition can thus be written as $Li_{1+x}[Li_{0.2}Mn_{0.2}Co_{0.2}Ni_{0.4}]O_{2+x}$. XRD measurements were performed and no notable Li_2O impurity was detected. The structure was also layered and no cubic tendencies were observed. The structure was best identified as *C*2/*m*, same as that for Li_2MnO_3. Samples were again washed in ethanol and ICP measurements showed only a slight loss of Li, but Li content increased as x increased. Neutron diffraction measurements showed a Li rich *C*2/*m* structure and possible new Li sites were investigated. XRD and ND results also showed that a composition of $M_{0.8}$ to O_2 was maintained, indicating excess O to have evaporated. X-ray absorption spectroscopy (EXAFS) revealed a change in the valence states of Ni and Co as *x* increased. Electrochemical experiments revealed capacities near or over 200 mAh g-1 and better cycle stability than previous stoichiometric samples. The oxygen generation plateau was still observed.

To further explore the excess oxygen synthesis conditions the composition of $Li_{1+x}[Li_{0.2}Mn_{0.2}Co_{0.2}Ni_{0.4}]O_{2+x}$ using only Li_2O_2 was synthesized using a high-pressure method with the addition of $KClO_4$ as an oxygen generator. XRD experiments revealed similar results to previous experiments of chapter 4 with the addition of a new impurity of $LiAu_3O_3$. ICP showed that washed samples had similar Li rich tendencies in their composition as those in chapter 4. ND measurements showed that a mix of *C*2/*m* phases and *R*-3*m* phases was more prominent than previous. Shifts in the valence states of Ni in particular were observed by EXAFS. Electrochemical experiments showed capacities above 200 mAh g^{-1} with good cycle stability. The higher amounts of R-3m phases and the higher performance suggest the ratio of the two phases is an important factor in the electrochemical performance.

The results of these experiments showed that the ratio of the two phases is an important factor in the electrochemical performance. Understanding of the overcapacity and its relation to the phase make up can provide direction for creating a battery cathode material for future generations.