

Title	コバルト系擬キャパシタの蓄電特性に関する第一原理解析
Author(s)	奥村, 健司
Citation	
Issue Date	2024-03
Type	Thesis or Dissertation
Text version	ETD
URL	http://hdl.handle.net/10119/19063
Rights	
Description	Supervisor: 本郷 研太, 先端科学技術研究科, 博士

Abstract

Pseudocapacitors using Cobalt Carbonate Hydroxide (CCH) electrode material are promising energy storage devices that provide a good balance between power density and energy density. However, achieving both cycle stability and capacitance has been a challenge. Therefore, attempts have been made to improve the properties by controlling the reaction site through morphology design. But the electrochemical reaction mechanism of the CCH electrode has not been fully clarified; deprotonation of the $\text{Co}(\text{OH})_2$ phase produced from the CCH phase has been proposed. On the other hand, the reaction mechanism for the CCH phase has not been proposed. Therefore, this research aimed to obtain a morphological design criterion for the improvement of energy storage properties from the first-principles electrochemical reaction analysis for CCH crystal. To evaluate the electromotive force (emf), it is necessary to identify all the atom configurations in the crystal structure, since the Co vacancies and hydrogen atom configurations in CCH crystals have not been experimentally identified. Therefore, we predicted the stable configuration pattern from first-principles screening based on symmetry and bonding theory. The validity of the deprotonation reaction inside the crystal was examined from the first-principles emf evaluation for the stable CCH crystal structure. The calculation results showed that the emf was more negative than -3 V, which is much more negative than the potential window of -0.7 V of electrochemical measurements in previous studies. Therefore, deprotonation inside the CCH crystal is unlikely to occur. Furthermore, based on the results of electrochemical reaction analysis in this study and previous studies on morphology control, the trade-off factors between cycle stability and capacitance were discussed. The previous studies on the control of storage properties of CCH electrode materials have reported that the capacitance decreases due to low surface area when the crystal growth time is long. On the other hand, high cycle stability has been reported. The opposite trend is reported when the crystal growth time is short. From the above, it is important to elucidate the factor by which high reactive surface area degrades cycle stability to achieve both cycle stability and capacitance. The degradation mechanism can be explained by the conclusion that the CCH phase does not contribute to the electrochemical reaction. If the precursor CCH phase has a high surface area, the CCH phase responsible for structural stabilization will decrease more, $\text{Co}(\text{OH})_2$ phase, which is responsible for electrochemical reactions, is expected to increase. Therefore, it is inferred that structural stability against charge-discharge is significantly degraded, but high capacity can be obtained. Moderate control of the ratio of CCH phase and $\text{Co}(\text{OH})_2$ phase in the CCH electrode by electrode surface area is considered important to achieve both cycle stability and capacitance.

Keywords: First-principles calculation, Density functional theory, Pseudo capacitor, Electrochemical reaction, morphology