

Reaction Mechanism study of Al³⁺ Ion Dissolved in Nano-size NiO Using ex-situ XAFS Measurement

N. Sonoyama¹, A. Koide², Y. Ogasawara¹, T. Tsukada¹, S. Yoshida¹ and K. Niki³

¹ Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, 466-8555, Japan.

² Institut de Physique de Rennes, UMR CNRS-UR1 6251, Université de Rennes-1, 35042 Rennes cedex, France

³ Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba, 263-8522, Japan.

sonoyama@nitech.ac.jp

Introduction

A new conversion type anode material for lithium ion battery utilizing the redox activity of aluminum (III) ion has developed. Conversion type materials are known to have a serious weak point as anode materials, that is the high reaction voltage in spite of its high capacity (over 600 mAh/g). This high reaction voltage originates in high redox potential of transition metal oxide such as NiO or CoO, those are known as representative conversion anode materials for lithium ion battery. In order to improve this high reaction voltage, it is effective to use oxides of light metal with lower redox potentials such as aluminum oxides, titanium oxide and so on. We have synthesized solid solution of nickel oxide and aluminum oxide with nano level particle size by calcination of Ni-Al layered double hydroxides (LDH). The fine structure of calcinated materials are determined by XRD and XAFS: Ni²⁺ and Al³⁺ ions are randomly locating metal ion sites of NiO with rock salt structure and cation vacancies are introduced to compensate the excessive charges brought by the aluminum ions. In this structure, electron and lithium ion are expected to be supplied via NiO type host structure and cation vacancies, respectively.

Experimental methods

Ni-Al LDH was synthesized by precipitation method and sintered at 400 °C. [1-2] The XAFS measurement at transition metal K edge was obtained at BL-9C at photon factory in High Energy Accelerator Research Organization in Japan.

Results and discussion

The charging capacity of the half cell with lithium metal counter electrode from 0.03 V to 1.5 V, that corresponds to the discharge capacity of the full cell was improved to 600 mAh/g, whereas that for pristine NiO was 230 mAh/g. This improvement of capacity in the lower voltage region is expected to originate in redox of aluminum ion. The redox activity of aluminum ion was confirmed by ex-situ XANES measurement at Al K edge. The absorption edge of aluminum ion shifted to lower energy direction with discharge from 1560 keV to 1556 keV. With charging, the absorption edge of aluminum shifted back to the initial position. This directly indicates the redox activity of aluminum ion during charge-discharge. This is the first report of anode material for lithium battery that utilizes redox of aluminum ion as far as we know.

Conclusion

The capacity of the conversion material was much improved by introducing Al³⁺ ion into NiO structure. This improved capacity is brought by the redox of Al³⁺ ion activated in Ni-Al oxide solid solution with cation vacancy.

Reference

[1] Z. Quan, et al., *J. Mater. Chem. A*, 2013, **1**, 8848.

[2] Z. Quan, et al, *Solid State Ionics*, **262** (2014) 128.