

Nano-size Metal oxides Synthesized from Layered Double Hydroxides as the Anode Materials for Lithium Ion Battery

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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. However, aluminum oxides are difficult to use as the electrode materials owing to the low electric and ionic conductivity. 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). In the previous studies, we have investigated the structure and electrochemical properties for the solid solution of NiO with TiO₂ or V₂O₅. [1] 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.

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 for lithium battery that utilizes redox of Al ion as far as we know.

In order to investigate the detailed reaction mechanism, ex-situ XRD and XAFS measurements were carried out. On the basis of these results, the reaction mechanism of Ni-Al binary metal oxide was concluded as follows. In the higher voltage discharge process (OCV-1.0 V), lithium intercalation into the cation vacancy and lithium ion adsorption to the surface of Ni-Al binary metal oxide with the partial redaction of nickel ion are proceeding. [1] In the lower voltage discharge (1.0-0.03 V), the conversion reaction proceeds with the reduction of Ni and Al ions. In the lower voltage charge process (0.03-1.0 V), only aluminum ion is oxidized to form an intermediate state, where aluminum ion makes complex with surrounding oxide ions. In the higher voltage charge process, nickel metal is oxidized to reform the Ni-Al binary metal oxide with the rock salt structure.

The cycle stability of metal oxides largely depended on the kind of transition metals. Co, Ni and Mn-oxides showed high stability, whereas the stability of Zn oxide was low. This reason is discussed in the presentation.

References

[1] Z. Quan, N. Erfe, Y. Hayashi, N. Sonoyama, *Solid State Ionics*, 62 (2014), 128-132.