

Nano-size multiple metal oxide anode electrodes synthesized from layered double hydroxides – Electrochemical reaction mechanism and surface morphology change during reaction with lithium ion



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ABSTRACT

Electrochemical properties of nano-size Ni–V, Ni–Fe and Mg–Fe multiple metal oxides, prepared from layered double hydroxides as precursors, for the anode electrode of lithium battery has been investigated using cyclic voltammetry, AC-impedance and ex-situ by SEM observation. In the CV curves of N–V multiple metal oxide, it became clear that the reaction voltage of vanadium–nickel oxide system shifted to lower voltage than non-doped NiO. AC-impedance and the morphology observation results that the electrochemical reaction of multiple metal oxides with lithium ion proceeds via the two-step reaction: the surface film formation above 1.0 V and the subsequent conversion reaction below 1.0 V.

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1. Introduction

Lithium secondary batteries are one of the great successes in modern electrochemical devices [1,2]. They have been the dominant backup power sources for mobile devices such as cellular phones and laptop computers. Recently, effective energy storage technology of the renewable energy such as wind or solar power attracts much attention. For the temporary stage of these electric powers, application targets of lithium batteries are expanding from consumer electronic device to large-scale electric vehicles and temporary energy storage systems to avoid the problems of exhaustion of fossil fuel and global warming. To satisfy the needs of new applications, batteries are required to be enhanced in terms of performance, especially high power density and high energy density with high cost performance.

Tarascon et al. reported that 3d transition metal oxides (MO, where M is Fe, Co, Ni, and Cu etc.) nanoparticles could reversibly react with lithium to achieve high theoretic capacities as high as 700 mAh g⁻¹ in 2000 [3–6]. The mechanism of the “conversion reaction” involves the formation and decomposition of Li₂O accompanied by a large amount of lithium ion reaction toward metal oxide nanoparticles as follows:



The metal oxide nanoparticles have been widely investigated as promising anodes materials for lithium secondary batteries for its high

capacity, and good rate property with low cost. However, the nano-size metal oxides have serious weak points as the anode material of the lithium battery. The most serious one is the very limited discharge capacity in the lower potential region with high hysteresis in potential between the discharge and the charge curves. This impairs the energy density of the battery fatally. To avoid the decrease in the energy density, some materials have been developed. Metal hydrides [7] and metal phosphides [8] have high capacity in the low voltage region with lower hysteresis in potential than that of metal oxides system. However, the use of these materials restricts the variation of materials, because the stable metal hydrides are limited, and raises the cost of the battery material.

In our previous studies, we have attempted at improving the electrochemical properties of nano-size metal oxide by the introduction of various metal ions with different valence numbers [9,10]. We have selected layered double hydroxides (LDHs), which can be expressed in the general formula of [M^{II}_{1-x}M^{III}_x(OH)₂](A^{m-})_{x/m} [11,12], as the precursors of nano-size metal oxide dissolved with other metal ions. Using the homogeneous solid solution of metal oxides (usually with rock-salt structure) prepared by calcination of LDHs at low temperature, we have reported that the voltage and capacity of nano-size metal oxides in the charging process can be improved. As the example, V⁵⁺ introduced Ni–V multiple oxide nano-particle shows a capacity of 821 mAh/g in charge process vs. Li metal counter electrode in the voltage range from 0.02 to 1.5 V.

In this study, we have examined the electrochemical properties of multiple metal oxides nanoparticles, Ni–V, Ni–Fe and Mg–Fe oxides synthesized from LDH precursors using cyclic voltammetry and AC-impedance measurement and discussed the reaction mechanism

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comparing the surface morphology change observed by the SEM measurement.

2. Experimental

The solid solution of multiple metal oxides, Fe^{III} dissolved MgO (Mg–Fe), Fe^{III} dissolved NiO (Ni–Fe) and V^{V} introduced nickel–vanadium oxide system (V–Ni) were prepared according to the method mentioned in the previous papers [9,10]. The ratio of divalent metal and other valent metals ($M^{\text{II}}:M^{\text{III}}$ or V) is 2:1 otherwise noted. The X-ray powder diffraction (XRD) patterns were recorded on Rigaku RAD-C with $\text{Cu K}\alpha$ radiation. The electrochemical properties of the multiple metal oxides were examined using CR 2032 coin cell at 25 °C. The electrode consisted of 32 wt.% of active material, 64 wt.% of acetylene black and 4 wt.% of PTFE binder. Lithium metal was used as anode and 1 M LiPF_6 in EC:DEC (3:7 v/v) was used as an electrolyte solution. Cyclic voltammetry was measured under the potential control by a potentiogalvanostat (Princeton Applied Research VersaSTAT 3) equipped with a function generator at the scan rate of 0.1 mV/s. The electrochemical impedance spectroscopy measurements of the cells were performed at

various electrode voltages using an impedance analyzer (Solatron 1260) over the frequency range from 10^{-2} Hz to 10^6 Hz with the applied voltage of 10 mV. The voltage imposed on the electrode was controlled by a potentiostat (Solatron 1280 C). Ex-situ observation of surface morphology of the powder samples was carried out by using a scanning electron microscope (SEM, Hitachi S-4800). The composite samples electrochemically discharged were taken out from the cell, rinsed with dimethyl carbonate and set in a specific cell in the Ar-filled glove box to avoid exposing samples to the air.

3. Results and discussion

In our previous study, extremely small particle size below 20 nm and large surface area over $110 \text{ m}^2 \text{ g}^{-1}$ of Mg–Fe, Ni–Fe and Ni–V oxides obtained by calcination of LDH precursors have been confirmed by TEM and BET measurements [9]. The XRD patterns of Mg–Fe and Ni–Fe oxides agreed with that of MgO with rock-salt structure, while the reflection of Ni–V oxide presented the pattern indexed for $\text{Ni}_3\text{V}_2\text{O}_8$ with orthorhombic $Cmca$ symmetry due to the high oxidation state of V^{5+} .

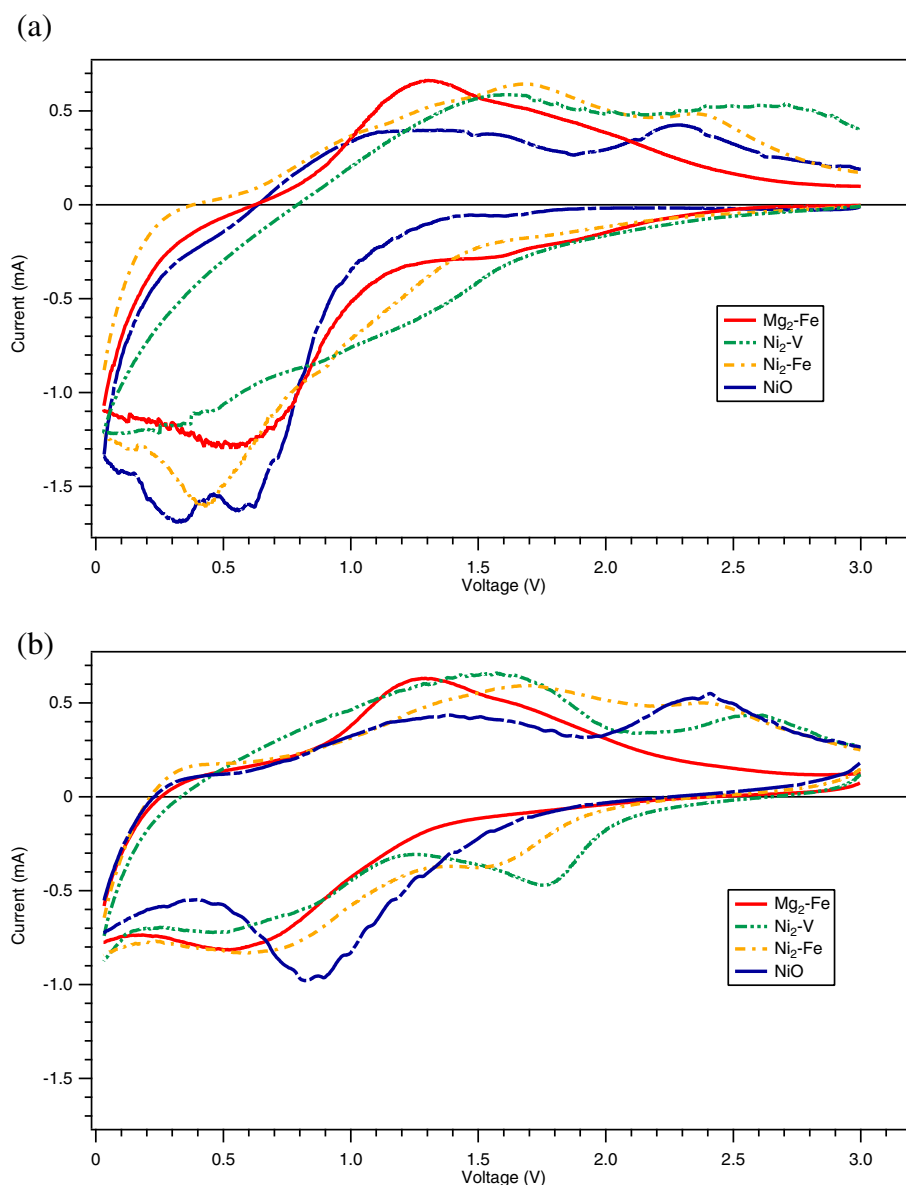


Fig. 1. Cyclic voltammograms of nickel oxide and multiple metal oxides in the (a) First and (b) second scans with the scan rate of 0.1 mV/s.

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