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Electrochemical properties of nano-sized binary metal oxides as anode electrode materials for lithium battery synthesized from layered double hydroxides

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ABSTRACT

Electrochemical performance of Ni-V, Ni-Fe and Mg-Fe oxide nano-sized particles obtained from layered double hydroxide (LDH) precursors were investigated as anode of lithium secondary batteries. These binary metal oxides showed very high reversible charge–discharge capacity for conversion reaction with lithium ion and good capacity retention. From the results of ex situ XRD and XANES measurements, it cleared the conversion reaction of the binary metal cation is occurring at the lower voltage range under 1.0 V. Especially for the Ni-V system, the lower hysteresis of voltage and the high capacity of 821 mAh/g in the lower voltage region were obtained owing to four step reduction of vanadium ion under 1.0 V.

1. Introduction

Lithium secondary batteries are one of the great successes in modern electrochemical devices [1,2]. They have been the dominant power sources for mobile devices such as cellular phones and laptop computers. Recently, the establishment of a low carbon society, which is based on clean and sustainable energy, has gradually become a worldwide topic. The development of pure electric vehicle (EV) and plug-in hybrid electric vehicle (plug-in HEV) plays a key role in reducing CO_2 emission and addressing the crisis of fossil energy source exhaustion. In addition, the effective energy storage technology of the renewable energy such as wind or solar power is also very important for the efficient usage of electric power. To satisfy the needs of new applications, batteries are required to have good performance, especially in high energy density and high cost performance.

Graphite is the main anode electrode for the current commercial lithium ion batteries because of its low redox potential and good cycle performance. However, the theoretical capacity of 370 mAh g^{-1} was strictly limited by amount of crystallographic sites, and this value cannot afford the high energy density of the next generation battery. It is well known that metal oxides show much higher capacity ascribed to different reaction mechanism, accompanying with multistep redox of transition metal ions ($M^n/M^{n+x}, x \geqq 1$). Recently, Tarascon et al. reported that 3*d* transition metal oxides (*M*O, where *M* is Fe, Co, Ni, Cu, etc.) nano-sized particles can reversibly react with lithium to achieve high capacities as high as 700 mAh g^{-1} [3–6]. The mechanism of the "conversion reaction" involves the formation and decomposition of Li_2O accompanied by reaction of the metal oxide nano-sized particles with two times of lithium ions in the following equation.

$$MO + 2Li^+ + 2e^- \Leftrightarrow Li_2O + M \quad (1)$$

The metal oxide nano-sized particles have been widely investigated as promising anodes for lithium secondary batteries with high capacity and good rate property. However, the cyclability of cheap metal oxides, such as FeO, NiO and CuO, are still insufficient for practical application. The investigation in conversion reaction of binary metal oxides is limited because the synthesis of the many structures of binary or ternary metal oxides requires high temperature and preparation of nano-sized particle is not easy. The development of nano-sized binary or ternary metal oxide system with various kinds of metal ions may solve the problems in the capacity and cycle stability. For example, the addition of metal ion with high valence number will improve the capacity and its reaction voltage may be changed by this approach.

For the development of binary systems, the formation of uniform and well-dispersed nano-sized particles will have a key for excellent electrochemical performance of nano-sized electrode materials. Generally, these nano-sized particles tend to aggregate together or bring about the crystal growth during the annealing process, which directly harm the functionality of nano-sized particles. To prevent undesired crystal growth and maintain the shape of nanostructure, special synthesis processes and expensive chemicals are applied even for the single metal oxide systems. For example, nano-sized γ-Fe_2O_3 was synthesized by mild oxidation of $Fe(CO)_5$, which needs five-step complicated reaction and many reagents such as $Fe(CO)_5$, octylether, oleic acid and so on [7,8]. This kind of synthesis method is not suitable for the practical

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Table 1
The composition, particle size, hysteresis in voltage during charge–discharge and charge capacity under 1.5 V for binary metal oxides.

	Composition of samples	Particle size (nm)	Hysteresis (V)*	Charge capacity under 1.5 V (mAh g^{-1})
Ni-V oxide	$Ni_{0.48}V_{0.21}O$	20	0.79	821.3
Ni-Fe oxide	$Ni_{0.47}Fe_{0.35}O$	9.0	0.93	549.0
Mg-Fe oxide	$Mg_{0.57}Fe_{0.29}O$	14	1.06	549.3
NiO	—	30	1.2	230

* Hysteresis was represented as voltage gap between 1 V of discharge and the voltage value that was obtained at same capacity on charge curve.

use because the complicated preparation process for these materials raises its production cost.

Layered double hydroxides (LDHs), which can be expressed in the general formula of $[M^{II}_{1-x}M^{III}_{x}(OH)_2](A^{m-})_{x/m}$ [9,10] are promising precursor that can derive the expected nanostructured materials because nano-sized binary metal oxide can be obtained by simple calcination at the low temperature. Abundant kinds of metal cation and anion can be used as the component of the LDH, and the synthesis method of LDH is simple and costly low. The calcination of LDH at low temperature is said to form the homogeneous solid solution of metal oxides (usually in rock-salt structure), which preserves the composition of former LDHs with extremely small particle size and large specific surface area [11,12]. We have determined the structure of the calcinated LDHs to be the solid solution of binary metal oxides by using EXAFS analysis and found that these materials act as the lithium intercalation materials [13,14].

In this study, the latent faculties of binary metal oxide nano-sized particles, Ni-V, Ni-Fe and Mg-Fe oxides synthesized from LDH precursors were examined as anode electrode for lithium secondary batteries by comparing the single metal oxide NiO synthesized in the similar procedure to the binary metal oxide systems and the reaction mechanism is also investigated.

2. Experiment

The preparation of the precursors of Mg-Fe, Ni-Fe and Ni-V LDHs and binary metal oxides was mentioned in the previous reports [13,14]. Nano-sized NiO was used as a standard sample of usual metal oxides. NiO was synthesized by a co-precipitation method using nickel nitrate as starting materials. An aqueous solution containing 1 M NaOH and 0.1 M Na_2CO_3 was added dropwise into the aqueous solution containing Ni^{2+}. NiO was obtained by the calcination of precipitation at 300 °C for 12 h. The X-ray powder diffraction (XRD) patterns were recorded on Rigaku RAD-C with Cu Kα radiation. The composition of samples was determined by a multi-type inductively coupled plasma emission spectrometer (Shimadzu ICPE-9000). X-ray absorption spectroscopy measurements were performed at the BL-7C beam line with the electron storage ring operating at electron energy of 2.5 GeV and a stored current of 450 mA using the Si (111) monochromator at the High Energy Accelerator Research Organization. The electrochemical performance of the binary metal oxides was examined using CR 2032 coin cell at 25 °C. To measure accurate voltage profile, suppressing the effect of overvoltage, we added larger amount of conductive additive than the

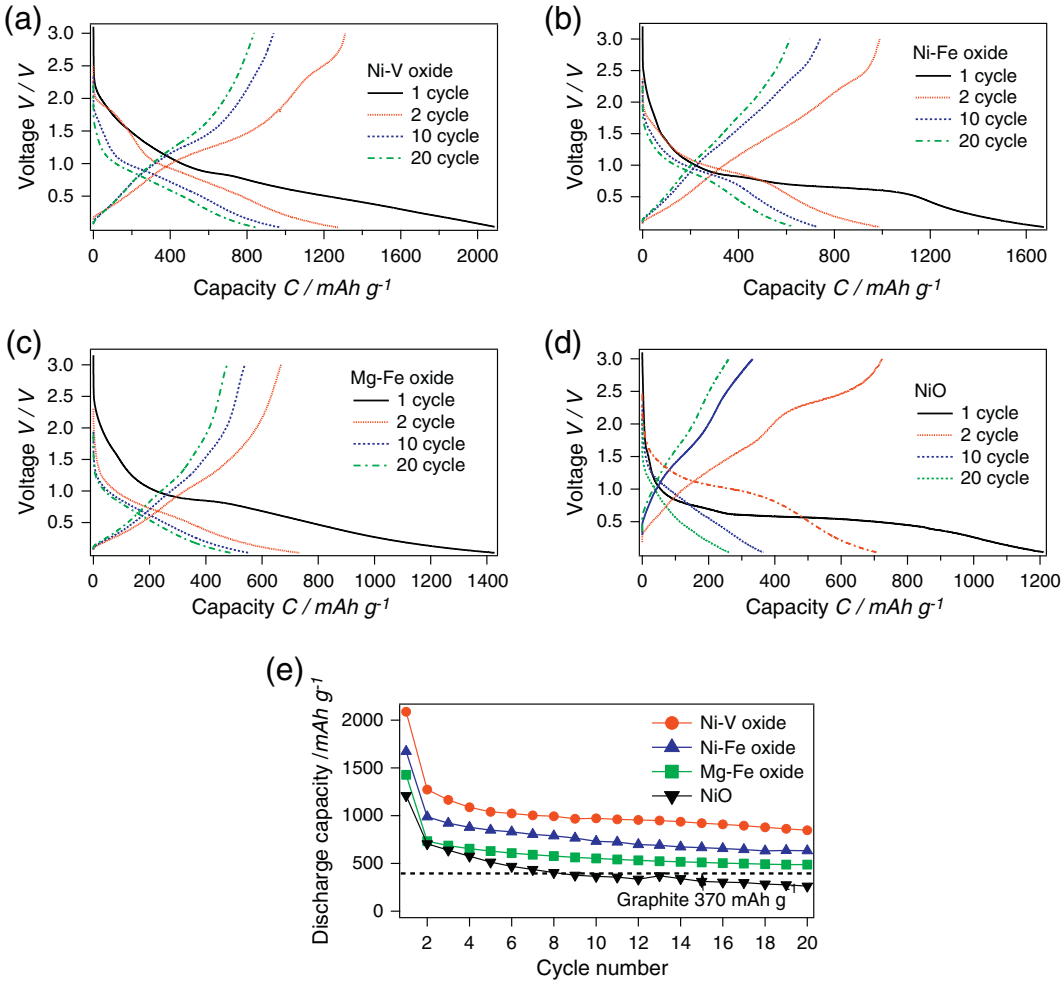

Fig. 1. The charge–discharge curves of (a) Ni-V, (b) Ni-Fe, (c) Mg-Fe oxides (d) NiO at the voltage range of 3–1.0 V and (e) relationship between discharge capacity and cycle number.

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