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Short communication

Effects of inorganic salts on the morphological, structural, and electrochemical properties of prepared nickel-rich $Li[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$

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HIGHLIGHTS

- Choosing inorganic salts plays a critical role in electrochemical performances.
- $Li[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$ is synthesized using various inorganic salts.
- Sulfate induces a large amount of void channel over the secondary particles.
- $Li[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$ material by sulfate shows the best cycling performances.

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ABSTRACT

The cathode active materials $Li[Ni_{0.6}Co_{0.2}Mn_{0.2}]O_2$ are synthesized using different inorganic salts, sulfate [$NiSO_4\cdot6H_2O$, $CoSO_4\cdot7H_2O$, $MnSO_4\cdot H_2O$], nitrate [$M(NO_3)_2\cdot6H_2O$ (M = Ni, Co, Mn)] and acetate [$M(CH_3COO)_2\cdot4H_2O$ (M = Ni, Co, Mn)]. The X-ray diffraction (XRD) patterns indicate that sulfate and nitrate starting materials formed a well-ordered hexagonal α-$NaFeO_2$ layered structure (space group: 166, $R\bar{3}m$). However, acetate starting material is led to a poorly layered structure compared to the other materials. Field emission scanning electron microscope (FE-SEM) images show that sulfate and acetate starting materials formed nano-sized primary particles with a size of about 200–500 nm and 300 nm, and void channels. However, the primary particles with a size of 300 nm from nitrate starting material agglomerate together to form micro-sized secondary particles. The initial discharge capacities of the sulfate, nitrate, and acetate starting materials are 138.3, 142.4, and 135.9 mAh g^{-1} at 1 C-rate in the voltage range 3.0–4.3 V vs. Li/Li^+, respectively. The discharge capacity retentions of sulfate, nitrate, and acetate starting materials are 92.5%, 63.9%, and 78.1% at 1 C-rate after 50 cycles, and 83.2%, 48.0%, and 71.7% at 6 C-rate after 100 cycles, respectively.

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1. Introduction

Rechargeable lithium ion batteries have been widely investigated as power sources for electronic devices such as cellular phones and laptop computers. Furthermore, higher energy density, longer cycle life, and better safety are necessary battery improvements for the development of hybrid electric vehicle (HEV), plug in hybrid electric vehicle (P-HEV), zero-emission electric vehicle (EV), and energy storage system (ESS), which can accumulate a large amount of the energy generated from wind power and solar cell plants [1–5].

In the last few years, lithium cobalt oxide has been widely used and investigated as a cathode active material because of its high coefficient of lithium ion diffusion and ease of processing. However, lithium cobalt oxide has several disadvantages such as toxicity, high cost, and poor rate capability. In addition, high energy and power density are required for large-scaled devices like EVs and ESS. Thus, many research groups have focused on finding new cathode materials that can provide high power and energy density for lithium ion batteries [6–8].

Among existing cathode materials, Ni-rich materials, $Li[Ni_{1-x-y}Co_xMn_y]O_2$ ($1-x-y\geq0.5$), are the most promising candidates for applications of EVs and ESS due to their excellent cycling ability, high specific capacity, relatively low toxicity, and good rate capability [9–12]. There are various inorganic synthesis methods such as the sol–gel process, hydrothermal synthesis, solid state reactions, and

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co-precipitation to prepare Ni-rich cathode materials [32,33]. Among these methods, co-precipitation has been widely used because it allows the uniform and homogeneous distribution of elements in particles and materials can be prepared on a large scale [13–18]. In co-precipitation, there are many factors that affect the physical properties of the product such as pH, temperature, agitation velocity, shape of reactor, feed rate, and starting materials, since the complex reactions are affected by various conditions that form the stabilized product [34]. In particular, anions of inorganic salts have an effect on the morphological and structural properties by changing the zeta potential and atmosphere of particles in solution [19–21].

In this study, Li[$Ni_{0.6}Co_{0.2}Mn_{0.2}$]O_2 cathode materials are synthesized by the co-precipitation method. The effects of different inorganic salt starting materials such as sulfate, nitrate, and acetate compounds on the morphological, structural, and electrochemical properties of the product Li[$Ni_{0.6}Co_{0.2}Mn_{0.2}$]O_2 were investigated.

2. Experimental

2.1. Synthesis of Li[$Ni_{0.6}Co_{0.2}Mn_{0.2}$]O_2

The $Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$ precursor was synthesized by co-precipitation in the following manner. Three inorganic salts, sulfate [$NiSO_4 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$, $MnSO_4 \cdot H_2O$], acetate [$M(CH_3COO)_2 \cdot 4H_2O$ (M = Ni,Co,Mn)], and nitrate [$M(NO_3)_2 \cdot 6H_2O$ (M = Ni, Co, Mn)], were employed. First, the metal salts (mol.% of Ni:Co:Mn = 6:2:2) were dissolved in distilled water with a total concentration of 2 mol L^{-1}, and the solution was pumped into a continuously stirred tank reactor. 4 mol L^{-1} NaOH and 1 mol L^{-1} NH_4OH solutions were simultaneously fed into the reactor. The solution was maintained at 50 °C under vigorous stirring for 12 h, and the pH value (pH = 11.0 ± 0.2) of the solution in the reactor was carefully controlled by the rate of NaOH addition. After the reaction, the precursor $Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$ was filtered, thoroughly washed, and then dried at 110 °C for 5 h. The obtained precursor was mixed with excess LiOH (mol.% of Mn + Co + Ni):Li = 1:1.05) to account for evaporation of lithium at high temperature. Finally, the mixture was sintered at 470 °C for 5 h and calcined at 850 °C for 5 h in air at a heating rate of 5 °C min^{-1}.

2.2. Preparation of the 2032 type coin cell

For fabrication of cathode electrodes, the obtained cathode active material, Li[$Ni_{0.6}Co_{0.2}Mn_{0.2}$]O_2 powder, was mixed with carbon black and polyvinylidene difluoride (PVdF) in wt.% of 85:7.5:7.5 in N-methyl-2-pyrrolidone solvent. The obtained slurry was laminated on Al foil and then dried at 120 °C for 5 h. A 2032 type coin cell was fabricated as a half-cell system using the obtained electrode as the cathode and lithium metal as the anode. A Celgard 3501 microporous membrane was used as a separator, and the electrolyte was 1.15 M $LiPF_6$ in ethylene carbonate:ethyl methyl carbonate = 3:7 vol.%.

Table 1
Structural parameters of Li[$Ni_{0.6}Co_{0.2}Mn_{0.2}$]O_2 samples made by different inorganic salts.

Samples	a (Å)	c (Å)	c/a	Volume (Å^3)	I_{003}/I_{104}[a]
Sulfate	2.8735	14.2198	4.9486	101.6812	1.5936
Nitrate	2.8684	14.2043	4.9520	101.2142	1.5012
Acetate	2.8697	14.2239	4.9566	101.4421	1.2757

[a] I/I_{003104} is the ratio of the intensities of the (003) and (104) peaks.

2.3. Characterization

The crystalline structure of prepared powders was analyzed by XRD (D8 Advance, Bruker) employing Cu Kα radiation. XRD data were obtained at $2\theta = 10°–80°$ with a step size of 0.02°. The TOPAS Rietveld program was applied to analyze the powder diffraction patterns. The stoichiometric ratio at the powder surface was determined using X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Electron). Surface morphology and particle size were observed using FE-SEM (Leo Supra 55, Carl Zeiss). Elemental composition was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Direct Reading Echelle ICP, Leeman).

Cycling performance of cathode material Li[$Ni_{0.6}Co_{0.2}Mn_{0.2}$]O_2 was evaluated in the range of 3.0–4.3 V in constant-current and constant-voltage mode using a battery cycler (BT-2000, Arbin). AC impedance measurements were performed using an electrochemical analyzer (Iviumstat, Ivium Technologies) over the frequency range of 1 mHz–100 kHz with an amplitude of 10 mV. Cyclic voltammetry (CV) was performed using an electrochemical analyzer (Iviumstat, Ivium Technologies) over 3.0–4.5 V at a scanning rate 0.1 mV s^{-1}.

3. Results and discussion

The XRD patterns for prepared $Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$ and Li[$Ni_{0.6}Co_{0.2}Mn_{0.2}$]O_2 with different sulfate, nitrate, and acetate

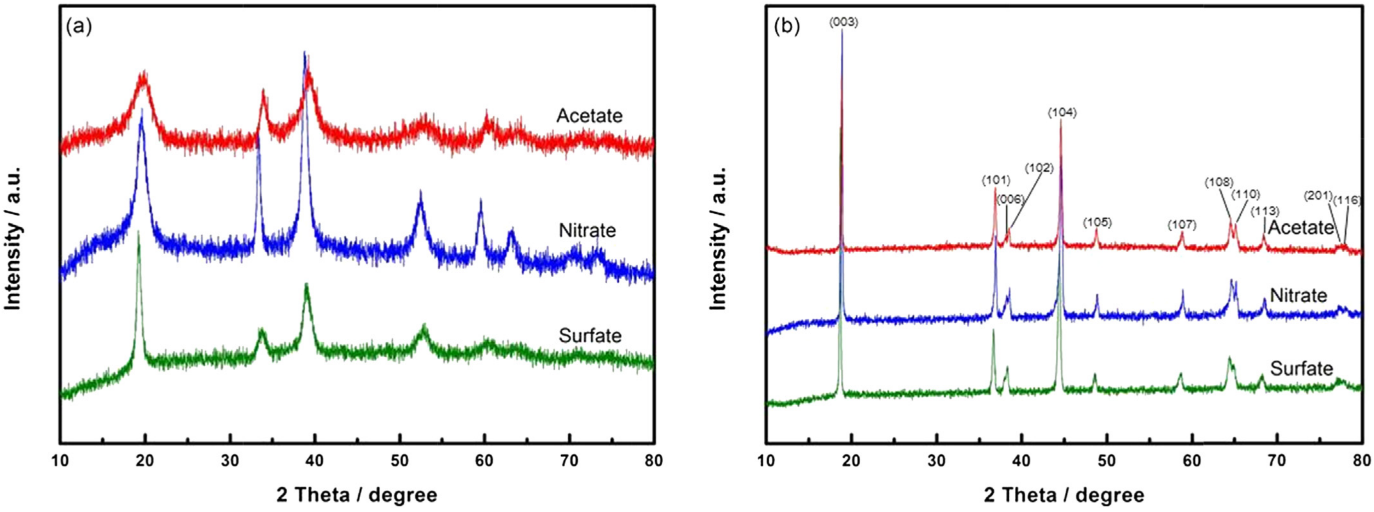

Fig. 1. XRD patterns of (a) $Ni_{0.6}Co_{0.2}Mn_{0.2}(OH)_2$ precursor samples and (b) Li[$Ni_{0.6}Co_{0.2}Mn_{0.2}$]O_2 calcined samples.

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