Synthesis and Electrochemical Properties of LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ Cathode Material

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LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ layer-structured compound was synthesized by the rheological phase reaction method. The structure and morphology of samples were characterized by x-ray diffraction and scanning electron microscopy. The particle size was distributed from 100 nm to 400 nm, depending on the synthesis temperature. The electrochemical properties of the samples were examined using a battery testing system. The results showed that the discharge specific capacities of the samples were strongly impacted by the synthesis temperature. The LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ synthesized at 850°C had a high initial discharge specific capacity (about 181 mA h/g at 0.1 C) and better electrochemical cycling performance compared to the other samples. (After 50 cycles, the discharge capacity was maintained at 170 mA h/g.) The reasons why the sample synthesized at 850°C showed outstanding electrochemical properties are also discussed.

Key words: Chemical synthesis, inorganic compounds, electronic materials, electrochemical properties

INTRODUCTION

Lithium-ion batteries, due to their low price, long cycle life, environmental safety, and high specific energy,1–4 have triggered the growth of the consumer electronics market and are now the power sources of choice for many popular devices, including hybrid electric vehicles, mobile phones, laptop computers, and other equipment. Layered LiCoO$_2$ is the predominant cathode material due to its high capacity and excellent cycling stability.5 As Co is an expensive and toxic element, however, and extracting more Li-ions from Li$_0.5$CoO$_2$ (by raising the charge cut-off voltage over 4.2 V) leads to a decrease in the lattice constant $c$ via a transition from the hexagonal to the monoclinic phase, thereby collapsing the structure, there are significant obstacles to its wider use. With increasing market demand, it is necessary to search for a new cathode material with lower cost, lower toxicity, and also greater ease of preparation to replace LiCoO$_2$.6,7 LiNiO$_2$ has higher specific capacity and is cheaper than LiCoO$_2$, but it is both electrochemically and chemically unstable, leading to difficulties for both synthesis and safety.8

One approach to improve the electrochemical performance is to partially replace cobalt with the elements nickel and manganese in the oxide compound. LiNi$_x$Co$_y$Mn$_{1-x-y}$O$_2$, a combination of the cathode cations Ni, Co, and Mn, has been reported as a promising positive material for rechargeable Li-ion batteries.9–11 These materials have the $x$-NaFeO$_2$-type structure. The valences of the nickel, cobalt, and manganese ions are 2+, 3+, and 4+, respectively, although only nickel ions and cobalt ions are electroactive. It was reported that

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specific capacity as high as 200 mA h/g could be attained when cells containing this cathode material were charged up to 4.6 V.\textsuperscript{12} LiCo$_{1/3}$Mn$_{1/3}$Ni$_{1/3}$O$_2$ has attracted much attention as a possible replacement for LiCoO$_2$ due to its multiple advantages, such as its high theoretical capacity, almost zero phase change when charged/discharged in the voltage range of 2.5–4.5 V, good thermal stability, low cost, and low toxicity.\textsuperscript{15–18} Its electrochemical performance is greatly influenced by its crystal structure, grain size, surface area, and porosity.\textsuperscript{16–18} In this paper, we present a novel synthesis method (the rheological phase reaction method) for layered LiCo$_{1/3}$Mn$_{1/3}$Ni$_{1/3}$O$_2$. The structure, morphology, and electrochemical properties of the as-prepared LiCo$_{1/3}$Mn$_{1/3}$Ni$_{1/3}$O$_2$ are also reported.

**EXPERIMENTAL**

The raw materials were LiOH·H$_2$O, Ni(Ac)$_2$·6H$_2$O, Co(Ac)$_2$·6H$_2$O, Mn(Ac)$_2$·6H$_2$O, and citric acid (CA). The molar ratio of reactants was \([n(\text{Li}):n(\text{Ni}):n(-\text{Co})]:n(\text{Mn}):n(\text{CA}) = 1.05:1/3:1/3:1/3:2.05\). A suitable amount of distilled water was added to the reactants, and the mixture was then milled for 4 h in a planetary mill. The rotation speed was 300 rpm, and the weight ratio of balls to powder was 20:1. After 4 h, the rheological phase mixture was reacted to form the precursor in an oven at 120°C for 24 h. Then, the mixed precursor was ground to a fine powder in an agate mortar. The precursor powder was heat-treated at 600°C for 6 h in air. After being cooled to room temperature, the intermediate LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ product was obtained. Then, the intermediate product was ground to a fine powder and calcined at different temperatures (800°C, 850°C, and 900°C) in air for 12 h to yield the different expected LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ samples, denoted as LNCMO-800, LCNMO-850, and LNCMO-900, respectively. X-ray diffraction (XRD) analysis of the samples was carried out on an x-ray diffractometer (Bruker D8-Advance, Germany), using Cu Kα1 radiation at room temperature in the range of 20 = 10°–80°, and the particle morphology was observed by scanning electron microscopy (SEM; JSM6510LV, Japan). The chemical composition of the as-prepared sample was examined by inductively coupled plasma (ICP) with atomic emission spectroscopy (ICP-AES; PLASPEC, USA).

The electrochemical performance of these samples was tested in a model test cell system. Positive electrodes were prepared by pressing mixtures of the active material (70%), acetylene black (20%), and polytetrafluoroethylene (PTFE) (10%) onto a nickel grid. Prior to being used, the positive electrodes were dried at 120°C in a vacuum furnace for 24 h. The electrolyte was a solution of 1 M LiPF$_6$ in ethylene carbonate and diethyl carbonate (1:1 by volume). The separator was Celgard 2400 porous polypropylene. The counter and reference electrodes were lithium foil. The model test cells were assembled in an argon-filled glove box. Charge–discharge tests were carried out at different current densities in the range of 2.5–4.5 V. Electrochemical impedance spectroscopy (EIS) measurements were conducted on an electrochemistry workstation.

**RESULTS AND DISCUSSION**

The real chemical composition was determined by ICP. The ratio of Li:Ni:Mn:Co of the obtained powder was about 1:1/3:1/3:1/3 for the samples synthesized at 800°C, 850°C, and 900°C, respectively. It is obvious that extended calcination leads to little loss of lithium. Since the oxygen lattice is a close-packed structure of the \(\alpha\)-NaFeO$_2$ type, the chemical formula of the samples could be represented as LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$. XRD results for the three LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ samples synthesized at 800°C, 850°C, and 900°C for 12 h are shown in Fig. 1. All of the diffraction peaks were indexed based on a hexagonal \(\alpha\)-NaFeO$_2$ structure with space group \(R3m\).\textsuperscript{23} No obvious impurity peaks are found. It can be clearly seen that the intensities of the peaks for the 850°C and 900°C samples are stronger than for the sample synthesized at 800°C. The lattice constants of the samples are shown in Table I. The lattice parameters of the samples decreased with increasing synthesis temperature. Higher synthesis temperature leads to an increase in the Ni(IV) oxidation state in the compound and, consequently, a smaller average ionic radius, \(R\), for the Ni ions (\(R_{\text{Ni(II)}} = 0.69\) Å; \(R_{\text{Ni(III)}} = 0.56\) Å, and \(R_{\text{Ni(IV)}} = 0.48\) Å). The smaller ionic radius for the higher synthesis temperatures may mainly account for the shrinkage in lattice constants.

It is well known that the particle size, particle size distribution, and morphology of a sample will directly influence the electrochemical performance of the electrode material. In order to elucidate changes in the morphology of the LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ powders, Fig. 2a–f shows SEM images of the LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ samples obtained at 800°C (a, b), 850°C (c), and 900°C (d, e, f).