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Development and characterization of layered $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_{1-x-y})\text{O}_2$ cathode materials for lithium ion batteries

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ARTICLE INFO

Article history:

Received 13 November 2015

Received in revised form

11 March 2016

Accepted 17 March 2016

Available online 8 April 2016

Keywords:

Li-ion batteries

Spray pyrolysis

Layered cathode materials

Rate capability and cycle life

ABSTRACT

The structure of the layered $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_{1-x-y})\text{O}_2$ in different amounts of x and y ranging between 0.2 and 0.6, have been synthesized and investigated by powder X-ray diffraction and electron microscopy techniques. In the current work spray pyrolysis was used to obtain spherical fine-sized morphology followed by heat treatment to obtain better electrochemical activity. The precursor powders were prepared using aqueous solution via spray pyrolysis. Synthesized samples were then heat treated at 850 °C. X-Ray Diffraction patterns of synthesized cathode materials showed well defined splitting of [006]/[102] and [108]/[110] diffraction peaks indicating layered structure and good hexagonal ordering. In this study, $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ (111), $\text{Li}(\text{Ni}_{0.2}\text{Mn}_{0.2}\text{Co}_{0.6})\text{O}_2$ (226), $\text{Li}(\text{Ni}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2})\text{O}_2$ (622) and $\text{Li}(\text{Ni}_{0.2}\text{Mn}_{0.6}\text{Co}_{0.2})\text{O}_2$ (262) were synthesized. The morphology of cathode materials was investigated by scanning electron microscopy and average crystallite size was measured to be between 0.2 μm and 0.6 μm . Moreover, particle sizes were verified by particle size measurement and transmission electron microscopy techniques. The electrochemical cells were cycled at 0.1C and 0.3C rate ($1\text{C} = 170 \text{mAhg}^{-1}$) and it was found that fast charging and discharging behavior were not sufficient. However, capacity retention after 32 cycles were determined to be 85.3% and 90%, for (111) and (262) samples, respectively.

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Introduction

Rechargeable lithium ion batteries are the key components of devices, especially for mobile applications as a power source. The most important requirements for this kind of application are energy density and cycle life. Electrode materials have an important effect on these properties, thus new cathode materials and structures are concerning issues [1].

LiCoO_2 has been adopted as the cathode material in commercial Li-ion batteries. However, capacity of cathode is limited to perform 50% of its theoretical capacity (140mAhg^{-1}) [2]. Also, toxicity and high cost of cobalt limit LiCoO_2 usage for large scale systems. Therefore, new cathode materials search has been started on related compound of LiMnO_2 due to its lower cost and environmentally – benign properties of manganese. On the other hand, there was another cathode material having the highest theoretical capacity which is

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<http://dx.doi.org/10.1016/j.ijhydene.2016.03.127>

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LiNi_{0.5}Mn_{0.5}O₂ among layered oxides. However, LiNi_{0.5}Mn_{0.5}O₂ cathode material suffers from 8 to 10% Li/Ni exchange which affects the high-rate performance of cathode material. To stabilize the layered structure, addition of Co has been found to be useful and a new compound Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O₂ has emerged [1]. Studies on the amount of Mn content showed that increasing amount of Mn causes faster capacity loss and poorer rate capability [3]. Furthermore, increasing the amount of Mn beyond 0.5 per formula caused spinel phase formation and induced larger particle size [4]. Studies related with Co element indicates that Co can stabilize the layered structure and suppress the migration of transition metal ions into the interlayer Li sites [5]. On the other hand, higher Ni content in Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O₂ is responsible for higher reversible capacity because of the main redox species of Ni [1]. In Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O₂ structure, cations have significant role due to their effect on electrochemical properties. Especially, Li/Ni cation exchange is quite important due to closer ionic radius of the species. In order to improve cycling performance of Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O₂ at high voltage, Cr³⁺ cations replacing Co sites were studied. The researcher reported that the capacity retention of undoped material was only 86.6% after 50 cycles. Whereas Cr doped sample exhibited capacity retention above 97% after 50 cycles [6].

Si doping was studied for Li(Ni_xMn_yCo_{1-x-y})O₂ cathode material. It was reported that Si element was easily doped up to about 10 at.% without any additional phase formation. The Si-doped material showed enhanced cycle life and rate capability besides the positive effects like increasing lattice parameters and stabilization of the electrochemical impedance [7]. In another work it is reported that, Li(Ni_{0.4}Mn_{0.4}Co_{0.2})O₂ showed excellent rate capability and reversible capacity ranging from 180 to 155 mAhg⁻¹ at current densities from 0.1 to 2.0 mAcm⁻². In the same study, Co was found to stabilize the layered structure and suppressed the migration of transition metal ions into the interlayer Li sites [8]. Replacement of Co element by Ti, Al and Fe had been studied in Li(Ni_{1/3}Mn_{1/3}Co_{1/3-y})O₂. Fe substitution exhibits lower capacity and poorer rate capability due to kinetic limitations resulting from an increase in the anti-site cation defect concentration whereas Ti and Al shows higher capacities compared to Fe. Effect of calcination temperature was also studied for Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O₂ which was calcined at 800–1100 °C. Fujii et al. found that surface area decreases by increasing temperature. There was no formation of impurity phases between 800 and 900 °C, however existence of spinel like phase was observed at 1000 °C. Besides, decreasing amount of Li, Li_x(Ni_{1/3}Mn_{1/3}Co_{1/3})O₂ (x ≤ 0.89), caused spinel like second phase and showed degraded electrochemical properties [9].

Yttrium doped Li(Ni_{1/3}Mn_{1/3}Co_{1/3})_{1-x}Y_xO₂ with x = 0.06 showed high discharge capacity and good cyclic capacity. Li et al. reported Y as a doping element caused defects in the structure and increased electronic conductivity, thus improved the Li⁺ kinetic behavior. It was also found that Y³⁺ ion can stabilize the layered structure [10].

In order to improve cycling performance of Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O₂ at high voltages, Mg²⁺, Cr³⁺ and Al³⁺ cations were studied in another study. These metals were used as doping elements by replacing Co element. It was shown that these doping elements have stable state when they are charged to

4.6 V. The capacity retention of the un-doped material was only 86.6% after 50 cycles. The capacity loss might be caused by the Co dissolution into the electrolyte at higher voltages. Cr doped sample showed no significant capacity fade with capacity retention above 97% after 50 cycles. On the other hand, Mg and Al exhibited an evident capacity fade during cycling and capacity retention was found as 82.1% and 76.4% for Mg-doped and Al-doped, respectively [6]. Li, Xu et al. studied Zn-doped Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O₂ cathode material with amount of 0.02 and 0.05 atomic ratio. Capacity loss was only 0.20% after 100 cycles and capacity was 142 mAhg⁻¹ at 3C. Zn-doped material showed reduced electrode polarization, decreased impedance and increased lithium ion diffusion with excellent cycling performance [11]. Therefore, it is for sure that doping elements have significant effect on electrochemical properties.

In this regard, layered Li(Ni_xMn_yCo_{1-x-y})O₂ cathode materials have been extensively studied as an alternative cathode searching for higher capacity, cycle life, rate capability and safety. Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O₂ cathodes exhibit higher capacity that of close to 200 mAhg⁻¹ with enhanced safety [12]. The high capacity can be associated with the improved chemical stability. However, the rate capability is the most important deficiency which should be improved for layered Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O₂ cathode materials. The thermal behavior of Li(Ni_{1/3}Mn_{1/3}Co_{1/3})O₂ with electrolyte is much better than that of commercial cathode material, LiCoO₂, for lithium ion batteries [9].

Production of Li(Ni_xMn_yCo_{1-x-y})O₂ cathode materials with spherical and smaller particle size is the aim of this study. It is well-known that properties such as morphology, specific surface area and the crystallinity have great effect on electrochemical properties. In the consideration of powder morphology, spherical powders with narrow size distributions show better electrochemical performance than powders with irregular shapes. Particle size and shape can easily be controlled in spray pyrolysis, therefore this technique has been chosen to obtain spherical and fine sized particles. In this study, different Li(Ni_xMn_yCo_{1-x-y})O₂ cathode materials were synthesized with optimized spray pyrolysis conditions and effects on electrochemical properties were investigated.

Experimental

The precursor powders were prepared using aqueous solution via spray pyrolysis. Li(Ni_xMn_yCo_{1-x-y})O₂ cathode materials were synthesized using aqueous solutions of lithium nitrate (LiNO₃), nickel (II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O), manganese (II) nitrate tetrahydrate (Mn(NO₃)₂·4H₂O) and cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O) with certain mole ratio of related compositions. The total concentration of the solution is 0.5 M with additives of citric acid and ethylene glycol. Spray pyrolysis system comprise of a droplet generator, reactor and powder collector. Solution was nebulized using an ultrasonic nebulizer operating at 1.7 MHz frequency. Droplets were then carried into the quartz tube reactor of 7 cm diameter, inside a three zone tube furnace by pure oxygen carrier gas. The flow rate of oxygen was 8 l/min and the reactor temperature was maintained 600 °C. The powders were collected by

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