Journal of Power Sources 196 (2011) 6710–6715

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Effects of manganese and cobalt on the electrochemical and thermal properties of layered Li[$Ni_{0.52}Co_{0.16+x}Mn_{0.32-x}$]$O_2$ cathode materials

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ARTICLE INFO

Article history:
Received 27 August 2010
Received in revised form 5 November 2010
Accepted 8 November 2010
Available online 13 November 2010

Keywords:
Coprecipitation
Stability
Interfacial resistance
Cathode
Lithium battery

ABSTRACT

We investigate the effects of the Co and Mn ratio on the structure, morphology, electrochemical properties, and thermal stability of Li[$Ni_{0.52}Co_{0.16+x}Mn_{0.32-x}$]$O_2$ cathode materials. Li[$Ni_{0.52}Co_{0.16+x}Mn_{0.32-x}$]$O_2$ (x = 0, 0.08, 0.16) cathode materials are prepared via high temperature calcination of LiOH and coprecipitated [$Ni_{0.52}Co_{0.16+x}Mn_{0.32-x}$]$(OH)_2$ hydroxides. From an X-ray diffraction investigation, the prepared materials have a well ordered O_3 type α-$NaFeO_2$ layer structure ($R\bar{3}m$). As the Co content (x) is increased, the initial discharge capacity increase slightly but it is accompanied by severe capacity fading during extensive cycling. Meanwhile, a small increase of Mn enhances the electrochemical stability at high temperature (55 °C) as well as the thermal stability. Electrochemical impedance spectroscopy reveals that manganese substitution is effective to reduce the resistance during cycling due to stabilization of the host structure.

1. Introduction

Lithium-ion batteries have become the state-of-the-art power source for electronic devices including laptop computers, cellular phones, and digital cameras. Even more important is the realization of high capacity batteries for hybrid and electric vehicles. In order to achieve this goal, the electrochemical properties of electrode active materials in addition to lower cost, longer cycle life, and better safety characteristics should be improved.

Over the past several years, layered Ni-rich Li[$Ni_{1-x}M_x$]O_2 (M = metal) materials have been intensively studied as an alternative cathode material for rechargeable lithium-ion batteries to replace lithium cobalt oxide ($LiCoO_2$) due to its drawbacks including toxicity, high cost, and instability at higher potentials (≥4.3 V vs. Li) [1,2]. Compared to $LiCoO_2$, Ni-rich Li[$Ni_{1-x}M_x$]O_2 has a large reversible capacity of approximately 200 mAh g^{-1} in the voltage range of 2.0–4.3 V vs. Li. However, Ni-rich Li[$Ni_{1-x}M_x$]O_2 has also disadvantages such as poor thermal stability and poor cycle life.

To improve the electrochemical properties of Ni-rich Li[$Ni_{1-x}M_x$]O_2, partial substitution of Ni with other metals has been performed. In particular, substitution of Co and Mn for Ni in Li[$Ni_{1-x-y}Co_xMn_y$]O_2 has resulted in substantially improved electrochemical properties and thermal stability without sacrificing the discharge capacity due to complete formation of a solid solution [3–6]. The capacity and thermal stability of layered Li[$Ni_{1-x-y}Co_xMn_y$]O_2 cathodes seem to be strongly dependent on the Co and Mn contents. Based on our previous report, the presence of tetravalent Mn in the structure leads to not only good electrochemical properties but also improved thermal stability [7].

For this reason, we investigated the effect of the Mn content on the electrochemical properties and thermal stability of Li[$Ni_{0.52}Co_{0.16+x}Mn_{0.32-x}$]$O_2$ (x = 0, 0.08, and 0.16) cathode materials for application in secondary lithium-ion batteries.

2. Experimental

Spherical Li[$Ni_{0.52}Co_{0.16+x}Mn_{0.32-x}$]$O_2$ (x = 0, 0.08, and 0.16) powders with various metal compositions (Li[$Ni_{0.52}Co_{0.16}Mn_{0.32}$]$O_2$, Li[$Ni_{0.52}Co_{0.24}Mn_{0.24}$]$O_2$, and Li[$Ni_{0.52}Co_{0.32}Mn_{0.16}$]$O_2$) were prepared via a co-precipitation method [8]. An aqueous solution of M (M = $NiSO_4{\cdot}6H_2O$, $CoSO_4{\cdot}7H_2O$, and $MnSO_4{\cdot}5H_2O$) was pumped into a continuous stirred tank reactor (CSTR, capacity of 4 L) under a N_2 atmosphere. At the same time, a NaOH solution (aq) and a NH_4OH solution (aq) as a chelating agent were also separately fed into the reactor. The reactor temperature was maintained at 50 °C for 20 h while closely monitoring and controlling the concentration, pH, temperature, and stirring

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doi:10.1016/j.jpowsour.2010.11.045

speed of the mixture during the reaction process. The obtained $[Ni_{0.52}Co_{0.16+x}Mn_{0.32-x}](OH)_2$ powders were filtered, washed, and vacuum dried at room temperature. Finally, the prepared hydroxides were mixed with LiOH and then calcined at 820 °C for 15 h in air. The chemical compositions of the synthesized materials were determined by atomic absorption spectroscopy (AAS, Vario 6, Analyticjena).

Powder X-ray diffraction (XRD, Rint-2000, Rigaku, Japan) using Cu-Kα radiation was applied to identify the crystal structure of the synthesized material. The FULLPROF Rietveld program was applied to analyze the powder diffraction patterns [9]. The morphologies of the as-prepared powders were observed using a scanning electron microscope (SEM, JSM 6400, JEOL, Japan).

The cathodes were fabricated using a mixture of prepared powders (85 wt.%), carbon black (7.5 wt.%), and polyvinlylidene fluoride in *N*-methyl-2-pyrrolidinon (7.5 wt.%). The slurry was applied on Al foil and dried in an oven at 110 °C. The electrode was roll-pressed and then dried at 120 °C overnight under vacuum prior to use. The electrochemical properties were tested by using coin-type R2032 cells with lithium metal negative and counter electrodes. The electrolyte solution was 1 M $LiPF_6$ in a 1:1 volume mixture of ethylene carbonate and diethyl carbonate (PANAX ETEC Co. Ltd., Korea). The cell assembly was carried out in an Ar-filled glove box.

Differential scanning calorimetry (DSC) experiments were carried out with the cathodes by fully charging the cells to 4.5 V versus Li and opening them in the Ar-filled dry box. After carefully opening the cell in the Ar-filled dry box, the measurements were carried out in a Pyris 1 Differential Scanning Calorimeter (NETZSCH-TA4, Germany) at a temperature scan rate of $5\,°C\,min^{-1}$ in the temperature range of 50–400 °C.

AC impedance measurements were performed using a Zahner Elektrik IM6 impedance analyzer over the frequency range of 5 mHz–5 MHz with an ac amplitude of 10 mV.

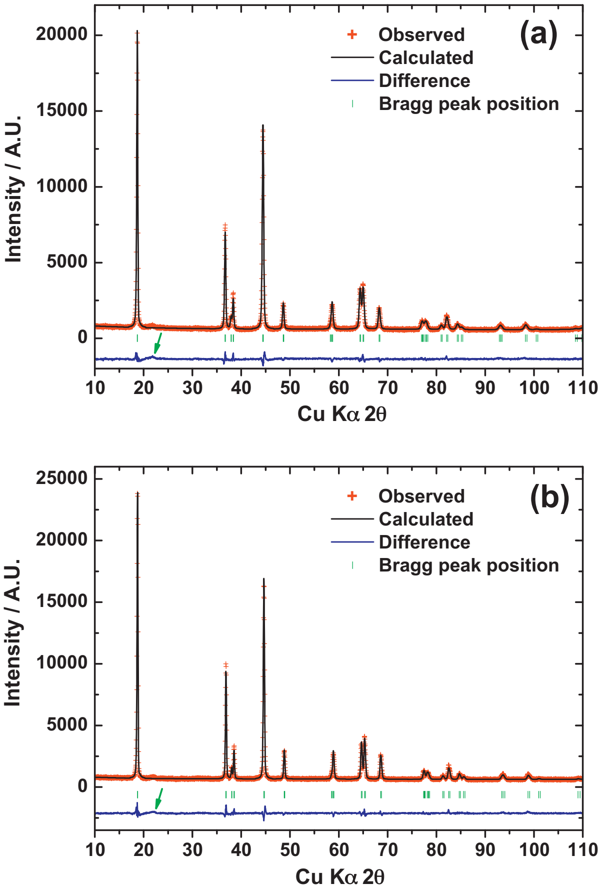

Fig. 1. Rietveld refinement result of XRD patterns of the as-synthesized (a) $Li[Ni_{0.52}Co_{0.16}Mn_{0.32}]O_2$ and (b) $Li[Ni_{0.52}Co_{0.32}Mn_{0.16}]O_2$ powders.

3. Results and discussion

Fig. 1 shows the Rietveld refinement results of the XRD patterns of the as-synthesized $Li[Ni_{0.52}Co_{0.16}Mn_{0.32}]O_2$ (Table 1) and $Li[Ni_{0.52}Co_{0.32}Mn_{0.16}]O_2$ powders. All peaks were indexed based on a hexagonal α-$NaFeO_2$ structure with a space group of $R\bar{3}m$. The splits of the (0 0 6)/(1 0 2) and (1 0 8)/(1 1 0) pairs for all samples indicate the formation of a layer structure. Interestingly, the splitting became sharper and the diffraction peaks moved to a higher angle with reduced Mn content, indicating lattice shrinkage by Co incorporation [10]. This characteristic results from the intrinsic properties of $LiCoO_2$, which exhibits a complete peak separation of the (1 0 8) and (1 1 0) peaks [11]. The AAS analysis reveals that the metal compositions of the obtained $Li[Ni_{0.52}Co_{0.16+x}Mn_{0.32-x}]O_2$ powder (x = 0–0.16) samples are similar to that of the starting composition, implying that the designated products were synthesized.

As seen in the XRD patterns in Fig. 1a and b, a small peak appeared at around 22° (2θ), indicative of a superstructure stemming from Ni^{2+} and Mn^{4+} arrangements in the oxide lattice. Thus, site exchange between Li and transition metal layers for both elements was allowed for the Rietveld refinement because the ionic radii of Li^+ (0.76 Å) and Ni^{2+} (0.69 Å) [12] are similar. The refinements resulted in good agreement between the observed and calculated patterns, which indicates that Co^{3+} and Mn^{4+} elements were incorporated into the transition metal layer, as expected. Furthermore, the resulting *a*- and *c*-axes monotonously decreased with increasing Mn content, as seen in Fig. 6. These phenomena result from the difference in the ionic radii of Ni^{2+} (0.69 Å), Co^{3+} (0.545 Å), and Mn^{4+} (0.53 Å) [12]. As described in Table 2, the divalent Ni content was also increased by decreasing trivalent Co and increasing tetravalent Mn in the transition metal layer. This result is mainly due to the decreased amount of Co because $LiCoO_2$ has a much lower occupation of Co^{3+} in the Li layer due to the difference in the ionic radii of Li^+ and Co^{3+}. Meanwhile, $Li[Ni_{0.5}Mn_{0.5}]O_2$, of which the valences of Ni and Mn are 2+ and 4+, respectively, usually has approximately 10% site exchange between Li and divalent Ni in the Li layer [13]. Thus, the increment of divalent Ni in the Li layer with increasing Mn content is understandable.

Fig. 2 shows SEM images of the synthesized $Li[Ni_{0.52}Co_{0.16+x}Mn_{0.32-x}]O_2$ powders (x = 0–0.16) after the thermal lithiation reaction at 820 °C for 15 h in air. The $Li[Ni_{0.52}Co_{0.16+x}Mn_{0.32-x}]O_2$ powders calcined following the optimum synthetic conditions resulted in dense and spherical particles with an average particle diameter of about 10 μm. The particle diameter of the $Li[Ni_{0.52}Co_{0.16+x}Mn_{0.32-x}]O_2$ powders is similar to the hydroxides, $[Ni_{0.52}Co_{0.16+x}Mn_{0.32-x}](OH)_2$. However, the thread-type primary particle of the hydroxide was completely changed to a rectangular primary particle.

Fig. 3a and b shows the first charge–discharge curves at a current density of $37\,mA\,g^{-1}$ (0.2 C) and continuous cycling results of the $Li/Li[Ni_{0.52}Co_{0.16+x}Mn_{0.32-x}]O_2$ powders (x = 0–0.16) cells measured in the range of 2.7–4.5 V at a current density of $93\,mA\,g^{-1}$ (0.5 C) at 25 °C, respectively. It is interesting to note that although the tetravalent Mn content, which is electrochemically inactive, increased, the resulting capacities were similar for all electrodes. It is thought that the content of Mn is likely to affect the oxidation state of Ni. In other words, a lower Mn content may induce the Ni valence to be higher, close to 3+, similar to $Li[Ni_{0.8}Co_{0.1}Mn_{0.1}]O_2$. Meanwhile, the higher concentration of Mn in the $Li[Ni_{0.52}Co_{0.16}Mn_{0.32}]O_2$