

Preparation of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ -based cathode materials for lithium batteries by a co-precipitation method

She-huang Wu*, Chi Wei Yang

Department of Materials Engineering, Tatung University, 40 Chungshan N. Rd, Sec.3, Taipei 104, Taiwan

Available online 26 April 2005

Abstract

$\text{LiNi}_{0.8}\text{Co}_{0.2-x}\text{Al}_x\text{O}_2$ ($0 \leq x \leq 0.1$) cathode powders were prepared with a novel co-precipitation method followed by heat-treating at temperatures between 500 and 900 °C. The electrochemical properties as cathode material for lithium batteries were predicted with XRD patterns and examined with capacity retention studies. Among the prepared samples, 800 °C heat-treated un-substituted $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ sample showed the best cycling performance. However, the initial specific discharge capacity decreases with increase amount of Al-substitution for the $\text{LiNi}_{0.8}\text{Co}_{0.2-x}\text{Al}_x\text{O}_2$ powders prepared with the same process. It may due to the increase in the amount of electrochemical inactive Al^{3+} and the increase in the hindrance of Li^+ ions diffusion by increasing Al^{3+} occupancy of interstitial tetrahedral 6c sites in the Al-substituted cathode materials.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Co-precipitation method; Al-substituted lithium nickel cobalt oxide; Lithium Battery; Cathode material

1. Introduction

Research into lithium nickel oxide has been gaining momentum because it shows much promise as a cathode material for lithium batteries due to its higher specific capacity ($>150 \text{ mAh g}^{-1}$) [1–3], lower maximum charging voltage [4], and lower cost than those of the commercialized LiCoO_2 . The chemical potential of lithium ion in LiNiO_2 is lower than in LiCoO_2 [5], which make the contact reduction of electrolytes on LiNiO_2 become less problematic. However, the commercial exploitation of the material is limited by the phase transitions occurred during the charge–discharge processes [1,2]. The resulting deterioration of the crystal structure leads to a high degree of capacity fading [6]. Moreover, the exothermic decomposition of LiNiO_2 in a highly charged state at elevated temperatures ($\sim 200^\circ\text{C}$) creates safety concerns for the devices that use it [7]. On the other hand, LiCoO_2 has been a popular cathode material primarily because of its good reversibility and ease of preparation. Hence, iso-structural solid solutions of the general formula

$\text{LiNi}_{1-y}\text{Co}_y\text{O}_2$ have been studied for their electrochemical properties. Because of its improved electrochemical properties, it is now generally recognized that $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ is a potential next-generation cathode material [8–10]. In order to further enhance the electrochemical properties and the thermal stability of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, powders with composition of $\text{LiNi}_{1-y}\text{Co}_{y-z}\text{Al}_z\text{O}_2$ were prepared and reported to be successful [11–18]. In this study, a novel and convenient co-precipitation method was employed to synthesize small particle-sized $\text{LiNi}_{0.8}\text{Co}_{0.2-z}\text{Al}_z\text{O}_2$ powders with $0 \leq x \leq 0.1$. The structural and electrochemical properties of the prepared powders were investigated. The effect of Al-substitution on the variation of the electrochemical properties of the powders prepared by this method was revealed from the results of capacity retention study.

2. Experimental

$\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and $\text{LiNi}_{0.8}\text{Co}_{0.2-y}\text{Al}_y\text{O}_2$ ($y = 0.01–0.1$) compounds were synthesized by a novel co-precipitation method with nickel nitrate, cobalt nitrate, aluminum nitrate, and lithium hydroxide as starting materials. According to

* Corresponding author. Tel.: +886 2 25922458; fax: +886 2 25936897.
E-mail address: shwu@ttu.edu.tw (S.-h. Wu).

the stoichiometric ratios, various aqueous solutions of Ni^{2+} , Co^{3+} , and Al^{3+} salts with total cationic concentration of 1 M were prepared. Precipitates formed after saturated aqueous LiOH solution was added to the solutions with volume ratio of 2:1. The precipitates were filtrated and calcined at 300 °C for 8 h followed by heat-treatment in flowing oxygen at temperatures between 500 and 900 °C for 8 h.

The crystalline structures of the prepared powders were investigated by an X-ray diffractometer (XRD-6000, Shmazu Co., Japan) with Cu K α radiation. The powder morphology was observed by a scanning electronic microscope (SEM, JSM-5600L, JEOL Ltd., Japan). The electrochemical properties of the prepared $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ -based powders as cathode materials for lithium batteries were investigated from the results of capacity retention studies with coin-type cells cycled between 3.0 and 4.3 V at 30 °C. The cells for these studies were assembled in an argon filled glove box with Li foil as anode, Celgard 2400 as separator, 1 M LiPF_6 in EC/DEC (1:1 in volume ratio) as electrolyte, and Al disk coated with various $\text{LiNi}_{0.8}\text{Co}_{0.2-y}\text{Al}_y\text{O}_2$ active materials as cathode.

3. Results and discussion

The dried precipitate prepared by the co-precipitation method was found to be a mixed hydroxide with composition close to the stoichiometric ratio of 1.0:0.8:0.2. The compositions of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders prepared at various temperatures for 8 h are listed in Table 1. Imperceptible effect of the heat-treatment temperature on the composition of the prepared samples is found as the temperature varying from 600 to 900 °C. The deviation of Li:Ni:Co atomic ratio from the tentative one can be ignored due to the limited precision of atomic absorption spectroscopy for bulk composition determination. Though, the lithium content decreases slightly as the heat-treatment temperature rising.

The XRD patterns of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders prepared at various heat-treatment temperatures for 8 h are shown in Fig. 1. Layered structure is observed exclusively in the powders without other phase. It is found that the intensities of the diffraction peaks increase with increasing heat-treatment temperature. The integrated intensity ratios of the (003) to (104) lines, R , are 0.76, 0.86, 1.30, 1.41, 1.73, and 1.72 for samples prepared at 500, 600, 700, 750, 800, and 900 °C for 8 h. The ratio had been recognized as a criterion

Table 1

The compositions of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders prepared at various heat treatment temperatures for 8 h

Molar ratio temp. (°C)	Li	Ni	Co
600	1.08	0.8	0.204
700	1.02	0.8	0.204
750	1.05	0.8	0.196
800	0.99	0.8	0.195
900	0.98	0.8	0.197

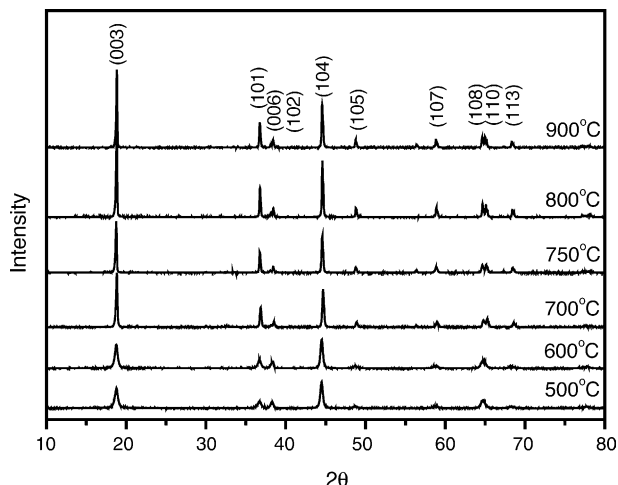


Fig. 1. The XRD patterns of $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders prepared at various heat-treatment temperatures for 8 h.

for the existence of cation mixing in the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders if it has value lower than 1.2 [5]. In addition, the separation between (108) and (110) lines could be used to judge the structure arrangement is ordered or not [19]. Moreover, the calculated lattice constant c increases with temperature of heat-treatment from 14.135 to 14.165 Å, whereas the lattice constant a remains almost constant of 2.86 Å. These values are close to the values reported previously [20]. The enlargement of the lattice constant c was realized as an enhancement of Li^+ ion diffusion in the layered structure [17]. From the results, it can be expected that the samples prepared at temperatures higher than 700 °C will show acceptable cycling performance for their R values higher than 1.2 and obviously separated (108) and (110) lines that suggests the samples may be free of cation mixing.

From the SEM photographs, shown in Fig. 2, it is found that the particle size increases by rising temperature of heat-treatment. The particle size increases gradually from 100 to 200 nm in 600 °C sample to 400–700 nm in 750 °C sample while significant particle size growth is found in 800 and 900 °C prepared samples.

The results of capacity retention studies, those were carried out with charging/discharging rate of C/10 and voltage window of 3.0–4.3 V at 30 °C, are shown in Fig. 3. As the prediction based on the results of XRD studies of the prepared $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders, the samples prepared at temperatures lower than 700 °C exhibits low initial specific discharging capacity of 30–40 mAh g^{-1} . The initial specific discharge capacity of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode increases as the temperature of heat-treatment is increased from 600 to 800 °C, however, no significant improvement in capacity loss is observed. Though the 900 °C prepared sample exhibits higher R value than others with well split (108) and (110) diffraction lines, it shows a low initial specific discharge capacity of 114 mAh g^{-1} . It may be attributed to the large particle size and the long diffusion distance of Li^+ ion that makes the intercalation/de-intercalation difficult. Lower

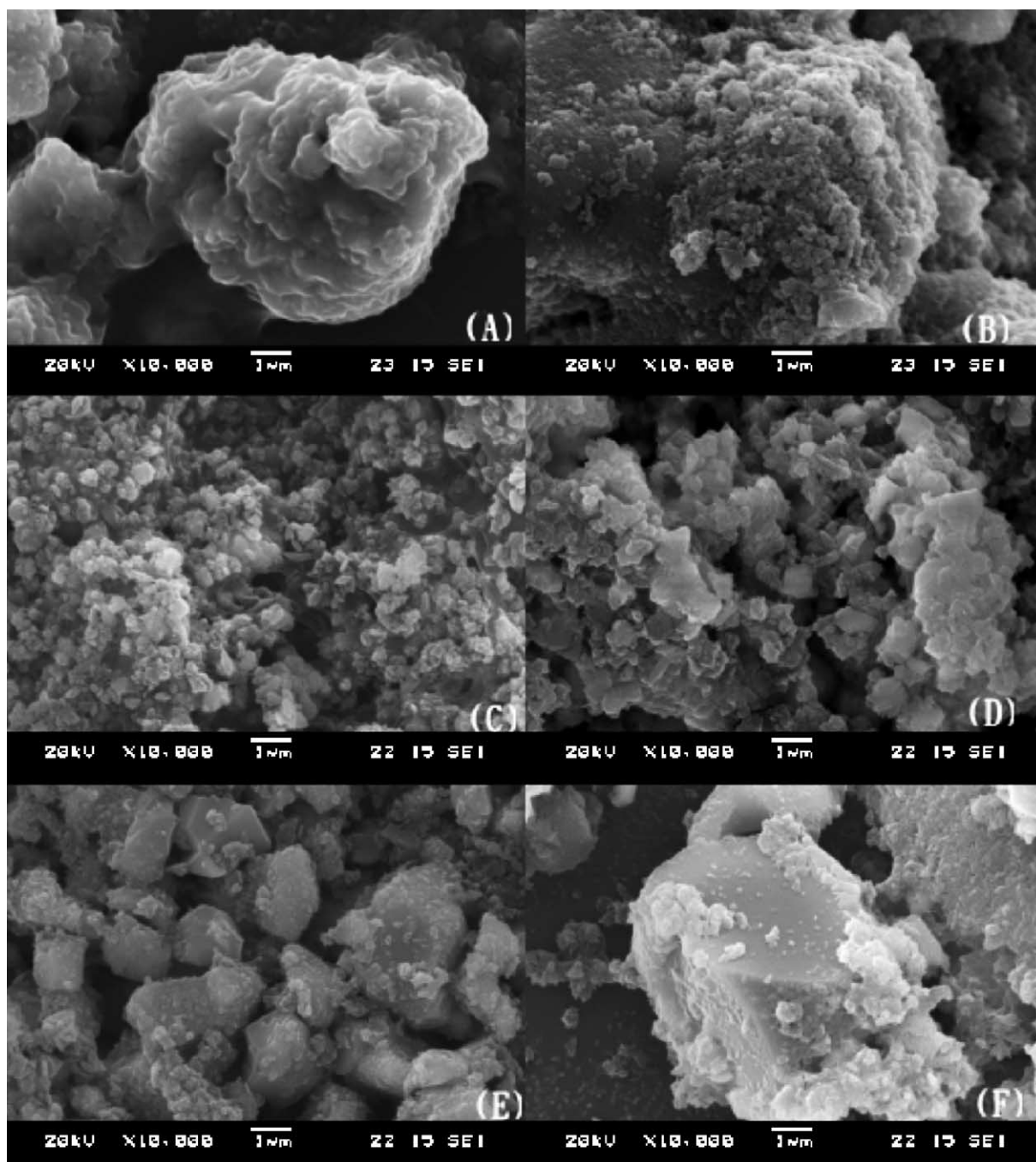


Fig. 2. SEM photographs of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders prepared at (A) 500, (B) 600, (C) 700, (D) 750, (E) 800, and (F) 900 °C for 8 h.

specific capacities than the expected values for the initial cycles are observed for some samples. That may be caused by insufficient electrolyte soaking of the cathode material. Among the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powders prepared at various heat-treatment temperatures for 8 h, the 800 °C prepared sample shows highest reversible discharge capacity. By extrapolation, the 800 °C prepared sample manifests initial discharge specific capacity of 185 mAh g^{-1} and capacity loss of 16% in 30 cycles. The performance is slightly poor than the reported result of a solid-state reaction prepared $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ pow-

der from LiOH and highly dispersive mixed oxide precursor, $\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$ [20].

The XRD patterns of the $\text{LiNi}_{0.8}\text{Co}_{0.2-x}\text{Al}_x\text{O}_2$ powders heat-treated at 800 °C for 8 h are shown in Fig. 4. The diffraction peaks corresponding to the layered structure are observed exclusively in the patterns of prepared powders with amount of Al-substitution, x , smaller than 0.1. It is also found that the intensities of the diffraction peaks increase with amount of Al-substitution and the integrated intensity ratios of (003) to (104) lines, R , are all greater than 1.2. Furthermore, (108)

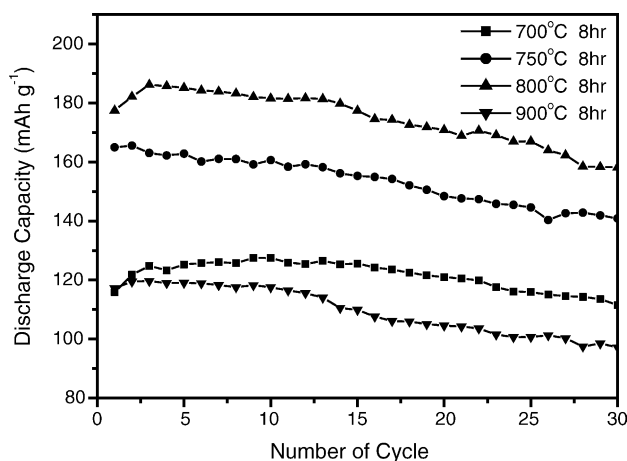


Fig. 3. Results of the capacity retention studies performed with C/10 rate and voltage window of 3.0–4.3 V at 30 °C for the coin-type cells with $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathodes heat-treated at various temperatures for 8 h.

and (1 1 0) lines are well separated for all patterns of the Al-substituted samples. Therefore, the 800 °C heat-treated $\text{LiNi}_{0.8}\text{Co}_{0.2-x}\text{Al}_x\text{O}_2$ powders, with $0 \leq x \leq 0.1$, are expected to show promising electrochemical properties as cathode material for lithium batteries from the observation of XRD patterns.

Variations of the lattice constants with amount of Al-substitution are plotted in Fig. 5. Whereas Al-substitution does not affect the lattice constant a , lattice constant c shows minimum value between $x = 0.01$ and 0.03 . The variation and the values of lattice constants are different from those of solid-state reaction prepared $\text{LiNi}_{0.8}\text{Co}_{0.2-x}\text{Al}_x\text{O}_2$ powders that the lattice constant a decreases from 2.868 to 2.862 Å as x increases from 0 to 0.10 while lattice constant c increases from 14.190 Å and becomes saturated at $x = 0.05$ [18]. The difference may be caused by the different preparation method and heat-treatment history. The decrease in lattice constant c at low Al-substitution may be attributed to the ionic radius of

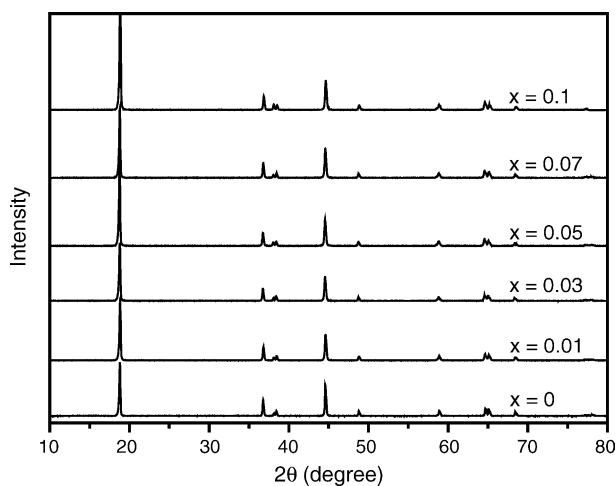


Fig. 4. The XRD patterns of $\text{LiNi}_{0.8}\text{Co}_{0.2-x}\text{Al}_x\text{O}_2$ powders heat-treated at 800 °C for 8 h.

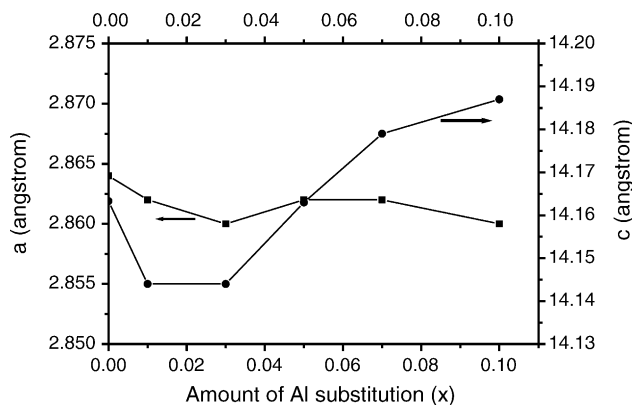


Fig. 5. Variations of the lattice constants with amount of Al-substitution, x , in the $\text{LiNi}_{0.8}\text{Co}_{0.17-x}\text{Al}_x\text{O}_2$ powders heat-treated at 800 °C for 8 h.

Al^{3+} in octahedral 3a site (0.054 nm) is slightly smaller than that of Co^{3+} (0.055 nm) [21], whereas the increase at high Al-substitution may be caused by the possible occupancy of Al^{3+} at the interstitial tetrahedral 6c sites that could lead to hindrance of Li^+ ion diffusion in the aluminum containing solid solution [17].

The results of capacity retention studies accomplished with C/5 rate between 3.0 and 4.3 V for $\text{LiNi}_{0.8}\text{Co}_{0.2-x}\text{Al}_x\text{O}_2$ powders are plotted in Fig. 6. The initial specific discharge capacity of the un-substituted $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ is 154 mAh g⁻¹. It decreases slightly to 148 mAh g⁻¹ as the amount of Al-substitution, x , increases to 0.03 and an abrupt decrease to 80 mAh g⁻¹ is found as x greater than 0.05. It is deviated from the suggestion that there is an optimum level of Al-substitution to provide improved cycling performance [11,18]. Nevertheless, it is consistent with the result reported by Madhavi et al. that the specific discharge capacity decreases with amount of Al-substitution as the cell were cycled at rates higher than 0.2C [13]. The capacity loss after 30 cycles also increases with increasing amount of Al-substitution. The decreasing in initial discharge capacity and increasing in capacity loss

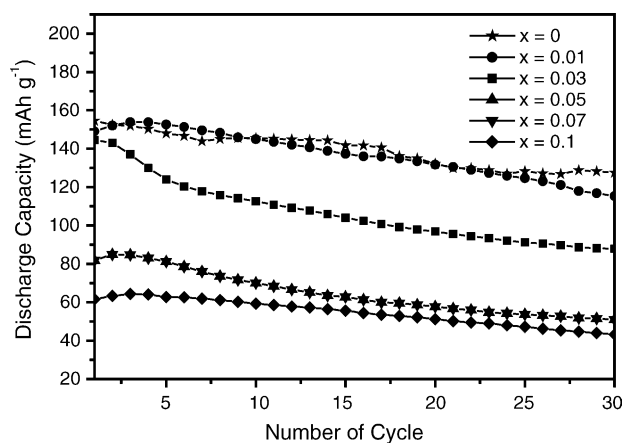


Fig. 6. Variations of the specific discharge capacity vs. cycle number performed at 30 °C with C rate of C/5 between 3.0 and 4.3 V for the cells with various $\text{LiNi}_{0.8}\text{Co}_{0.2-x}\text{Al}_x\text{O}_2$ cathode materials prepared at 800 °C for 8 h.

may be caused by the reducing lattice constant c at low Al-substitution level and Al^{3+} occupancy of interstitial tetrahedral 6c sites as the amount of Al-substitution is higher than 0.03. For both factors will lead to hindrance of Li^+ ion diffusion in the aluminum containing $\text{LiNi}_{0.8}\text{Co}_{0.2-x}\text{Al}_x\text{O}_2$ powders. Furthermore, the significant decrease of the reversible discharge capacity with increase of Al-substitution does also due to the electrochemical inactivity of Al^{3+} during the charge–discharge process [22].

4. Conclusions

Small particle sized $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and $\text{LiNi}_{0.8}\text{Co}_{0.2-x}\text{Al}_x\text{O}_2$ powders can be prepared easily and successfully by the novel co-precipitation method. Among the prepared samples, the un-substituted $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ powder heat-treated at 800°C for 8 h under flowing oxygen shows the best cycling performance. The cathode material shows initial specific discharge capacity of 185 mAh g^{-1} when cell was cycled with C/10 rate at 30°C . Partial Al-substitution for Co will hinder the Li^+ ion diffusion and thus reduce the cycling performance, though it is expected to exhibits improved electrochemical properties of cathode materials from XRD studies.

Acknowledgements

This research has been financially supported by Tatung University and Tatung Company.

References

- [1] T. Ohzuku, A. Ueda, M. Nagayama, J. Electrochem. Soc. 140 (1993) 1862.
- [2] W. Li, J.N. Reimers, J.R. Dahn, Solid State Ionics 67 (1993) 123.
- [3] H. Arai, S. Okada, H. Ohtsuka, M. Ichimura, J. Yamaki, J. Solid State Ionics 80 (1995) 261.
- [4] R.V. Moshtev, P. Zlatilova, V. Manev, A. Sato, J. Power Sources 54 (1995) 329.
- [5] T. Ohzuku, A. Ueda, M. Nagayama, Y. Iwakoshi, H. Komori, Electrochim. Acta 38 (1993) 1159.
- [6] C.C. Chang, P.N. Kumta, J. Power Sources 75 (1998) 44.
- [7] T. Ohzuku, A. Ueda, Solid State Ionics 69 (1994) 201.
- [8] C. Delmas, I. Saadoun, A. Rougier, J. Power Sources 43/44 (1993) 595.
- [9] J. Aragane, K. Matsui, H. Andoh, S. Suzuki, F. Fukuda, H. Ikeya, K. Kitaba, R. Ishikawa, J. Power Sources 68 (1997) 13.
- [10] J. Cho, Chem. Mater. 12 (2000) 3089.
- [11] S. Madhavi, G.V. Subba Rao, B.V.R. Chowdari, S.F.Y. Li, J. Power Sources 93 (2001) 156.
- [12] A.D. Epifanio, F. Croce, F. Ronci, V. Rossi Albertini, E. Traversa, B. Scrosati, Phys. Chem. Chem. Phys. 3 (2001) 4399.
- [13] S. Madhavi, G.V. Subba Rao, B.V.R. Chowdari, S.F.Y. Li, Solid State Ionics 152–153 (2002) 199.
- [14] W.-S. Kim, K.-i. Chung, Y.-K. Choi, Y.-E. Sung, J. Power Sources 115 (2003) 101.
- [15] S. Albrecht, J. Kumpers, M. Krufft, S. Malcus, C. Vogler, M. Wahl, M. Wohlfahrt-Mehrens, J. Power Sources 119–121 (2003) 178.
- [16] A.M. Kannan, A. Manthiram, J. Electrochem. Soc. 150 (2003) 349.
- [17] P. Kalyani, N. Kalaiselvi, N.G. Renganathan, M. Raghavan, Mater. Res. Bull. 39 (2004) 41.
- [18] CaoF H., B. Xia, N. Xu, C. Zhang, J. Alloys Compd. 376 (2004) 282.
- [19] Y. Gao, M.V. Yakovleva, W.B. Ebner, Electrochem. Solid-State Lett. 1 (1998) 117.
- [20] R. Moshtev, P. Zlatilova, I. Bakalova, S. Vassilev, J. Power Sources 112 (2002) 30.
- [21] Y.-M. Chiang, D.P. Birnie, W. David Kingery, Physical Ceramics: Principles for Ceramic Science and Engineering, Wiley, New York, 1997.
- [22] S.H. Park, K.S. Park, Y.K. Sun, K.S. Nahm, Y.S. Lee, M. Yoshio, Electrochim. Acta 46 (2001) 1215.