

Electrochemical properties of Co_3O_4 , $\text{Ni-Co}_3\text{O}_4$ mixture and $\text{Ni-Co}_3\text{O}_4$ composite as anode materials for Li ion secondary batteries

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Received 22 September 2003; received in revised form 19 December 2003; accepted 13 February 2004

Available online 17 April 2004

Abstract

By varying the synthetic temperature and time, Co_3O_4 with highly optimized electrochemical properties was obtained from the solid state reaction of CoCO_3 . As a result, Co_3O_4 showed a high capacity around 700 mAh/g and stable capacity retention during cycling (93.4% of initial capacity was retained after 100 cycles). However, its initial irreversible capacity reached about 30% of capacity. Several phenomenological examinations in our previous results told us that the main causes of low initial coulombic efficiency, that is, large initial irreversible capacity, were solid electrolyte interphase (SEI) film formation on surface and incomplete decomposition of Li_2O during the first discharge process. SEI film formation cannot be restrained without the development of a special electrolyte, and there has been little research on the proper electrolyte composition, whereas in our research, Ni had the catalytic activity to facilitate Li_2O decomposition. Thus, in order to improve the low initial coulombic efficiency of Co_3O_4 (69%), Ni was added to Co_3O_4 using two methods like physical mixing and mechanical milling. When adding the same amount of Ni, the mechanical milling showed the improvement in initial coulombic efficiency, 79%, but physical mixing had no effect. Finally, when the charge–discharge mechanism of Co_3O_4 was considered and the morphologies of $\text{Ni-Co}_3\text{O}_4$ mixture obtained by physical mixing and $\text{Ni-Co}_3\text{O}_4$ composite prepared by mechanical milling were compared, it was revealed that the initial coulombic efficiency of $\text{Ni-Co}_3\text{O}_4$ composite depends on the contact area between the Ni and the Co_3O_4 .

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Keywords: Li ion battery; Anode material; Transition metal oxide; Ni addition; Mechanical milling

1. Introduction

Since Li ion batteries became the commercial rechargeable battery, LiCoO_2 [1] has been utilized as the cathode material, and other kinds of transition metal oxides such as LiNiO_2 [2], LiMn_2O_4 [3] and recently, LiFePO_4 [4] have been tried as substitutes for LiCoO_2 . Therefore, transition metal oxides were just regarded as cathode materials, and their utility as anode materials was ignored. However, several researchers found that when Li ions are depleted in transition metal oxides, they show low potential, which means that transition metal oxides can be also used as anode materials for Li ion batteries. In addition, because of the capacity limit of graphite [5–7], the energy density of Li ion

battery cannot keep pace with that needed by recently developed portable electronic devices such as cellular phones, camcoders and laptop computers, whereas transition metal oxides have shown enough capacity to solve this problem [8]. So, transition metal oxides are now receiving considerable attention not only as cathode materials but also as anode materials. Among the various sorts of transition metal oxides, Co_3O_4 was reported to have the highest capacity and the most stable capacity retention during cycling [9]. Nevertheless, because its initial coulombic efficiency is too low to be utilized as an alternative anode material for Li ion batteries, it has not been commercialized yet [8,10].

Based on the previous research, we could expect two mechanisms to be mainly responsible for the low initial coulombic efficiency in Co_3O_4 . Li et al. reported that during the first charge process, solid electrolyte interphase (SEI) film was formed on oxide anode material by electrolyte decomposition, and while this film was retained during the

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first discharge process, the initial coulombic efficiency of oxide anode material got worse [11]. So, SEI film formation on surface seemed to be a candidate for the main cause of the low initial coulombic efficiency of Co_3O_4 . On the other hand, because transition metal oxides are charged or discharged by formation or decomposition of Li_2O , well known as an electrochemically irreversible material, incomplete decomposition of Li_2O during the 1st discharge process also seemed to be able to cause the deterioration of the initial coulombic efficiency in Co_3O_4 .

Hence, in this paper, we looked into the main cause of low initial coulombic efficiency for Co_3O_4 that shows the optimized properties as an anode material for the Li ion battery. In order to improve its initial coulombic efficiency, Ni was added to Co_3O_4 by physical mixing and mechanical milling.

2. Experimental

CoCO_3 was used as a precursor in this experiment. In order to obtain Co_3O_4 that shows the best electrochemical properties, CoCO_3 was heated at various temperatures between 500 and 800 °C with the change of synthetic times. The quantitative compositions of Co oxides from this process were confirmed by X-ray diffraction (XRD) patterns, and their approximate particle sizes and morphological properties were determined from scanning electron microscopy (SEM) images.

In order to improve the initial coulombic efficiency of Co_3O_4 , Ni– Co_3O_4 mixture and composite were manufactured. First of all, Ni– Co_3O_4 composite was obtained by mechanical milling metallic Ni powder with Co_3O_4 . For this process, SPEX 8000 mechanical miller was used and the ball to powder weight ratio was 7.65:1. To optimize the electrochemical properties of Ni– Co_3O_4 composite, the mechanical milling time was varied from 15 min to 2 h, and the amount of Ni addition was also changed from 5 wt.% of Co_3O_4 to 15 wt.%. Ni– Co_3O_4 mixture was prepared by adding 10 wt.% Ni powder to Co_3O_4 to be compared with the electrochemical performance of Ni– Co_3O_4 composite which was obtained using the mechanical milling.

To evaluate the electrochemical characteristics, electrodes were fabricated using the mixture which was composed of 72 wt.% active material (Co oxide powder or Ni– Co_3O_4 composite powder) and 20 wt.% acetylene black. A solution containing 8 wt.% polyvinylidene fluoride (PVDF) in *n*-methyl-2-pyrrolidinone (NMP) was added to the mixture. This as-prepared slurry was coated onto Cu mesh. After the electrode was dried at 110 °C for 2 h in vacuum (10^{-3} Torr), it was compressed under a pressure of about 180 kg/cm². The coin-type half cells were used for the charging/discharging experiment. (However, note that although the Co_3O_4 electrode is the cathode in the half cell, the charge and discharge process of Co_3O_4 electrode is named assuming that the Co_3O_4 electrode acts as the anode.) The assembly was

carried out in an Ar-filled glove box with less than 1 ppm each of oxygen and moisture. Then, Li metal foil was used as the counter electrode and reference electrode, 1 M LiPF_6 in ethylene carbonate and diethyl carbonate (1:1) was used as the electrolyte and Celgard 2400 was used as the separator.

The anode performance of the Co_3O_4 samples was measured over a range from 0.01 to 3.0 V (versus Li/Li^+) at 1C rate. The cycling tests were performed by using Toscat-3000u battery tester (Toyo System Corporation). To confirm whether Ni has a catalytic effect on Li_2O decomposition, cyclic voltammograms (CVs) (potential range: 0.01–3.0 V, scan rate: 1 mV/s) were obtained for Li_2O and the mixture of Li_2O –Ni (Li_2O was purchased from Aldrich). After oxidation or reduction of Li_2O , the cells were carefully opened in a glove box to recover the electrode, and the electrodes were subsequently rinsed in DEC to remove the residual LiPF_6 and finally dried at 80 °C. The dried electrodes were subjected to XRD in order to evaluate any structural changes of Li_2O during oxidation or reduction. XRD measurements were performed using monochromatic Cu K α radiation to observe either the structural changes of Li_2O or the crystallinity of Co oxide. The surface of specimens was observed by SEM analysis.

3. Results and discussion

3.1. The change of electrochemical properties of Co_3O_4 as a function of its synthetic temperature and time

Co_3O_4 was obtained by the solid state reaction of CoCO_3 in air. In order to make the specimen that shows the best electrochemical properties as an anode material, the synthetic time and temperature were changed. However, the structure and morphology of Co_3O_4 has nothing to do with the change of its synthetic time and so, Co_3O_4 specimens exhibited similar properties in terms of capacity and cycle life. On the other hand, when the synthetic temperature was varied, both the electrochemical properties and the phenomenological properties were changed. As shown in Fig. 1, when the synthetic temperature of Co_3O_4 increases, its crystallinity gets better. In addition, it is confirmed by Fig. 2 that an increase in the synthetic temperature results in an enlargement of the particle size of Co_3O_4 . (Because the melting point of Co_3O_4 is 900 °C, its synthetic temperature was only varied below this temperature.) Grugeon et al. reported that the particle size of Cu oxide used as an anode material for Li ion batteries was closely related to its electrochemical properties [12]. In detail, the larger particle size Cu oxide had, the better capacity and cycle life it showed. Because Co_3O_4 is charged or discharged by Li_2O formation or decomposition just like Cu oxide, the electrochemical properties of Co_3O_4 were also expected to be dependent upon its particle size. Fig. 3 shows that the increase of synthetic temperature improves the capacity of Co_3O_4 as well as its cycle life. Because an increase in the synthetic

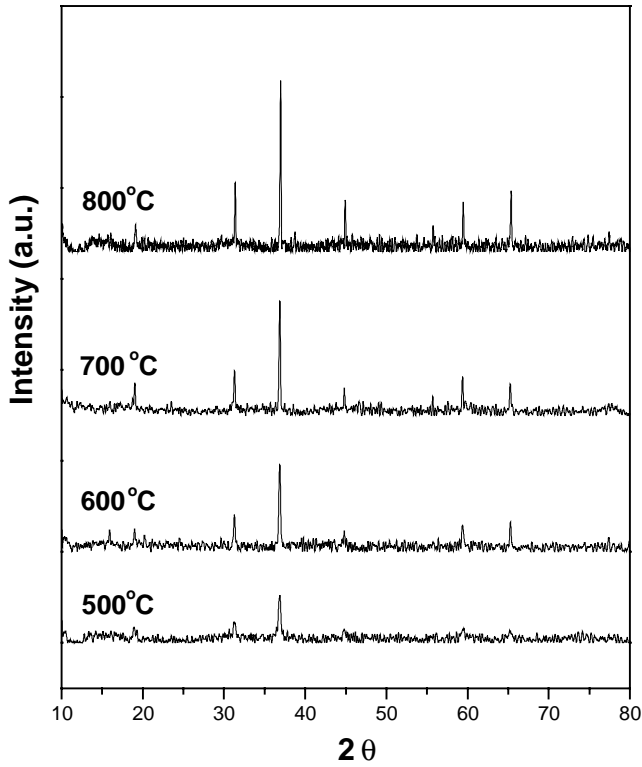


Fig. 1. XRD patterns of Co_3O_4 with respect to their synthetic temperatures.

temperature induced not only the enlargement of the particle size of Co_3O_4 , but also the increase of its crystallinity, it cannot be determined which of these factors is the main reason why the electrochemical properties of Co_3O_4 were

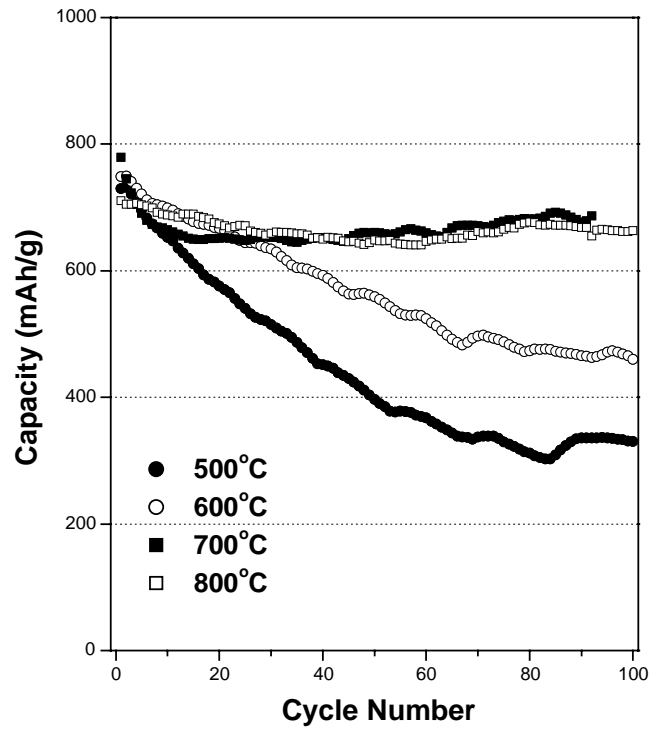


Fig. 3. Charge–discharge properties of Co_3O_4 according to their synthetic temperatures (charge–discharge experiment was conducted between 0.01 and 3 V at a rate of 1C).

improved with the increase of synthetic temperature. However, based on the charge–discharge mechanism of Co_3O_4 , the increase of particle size is more persuasive as the main reason than the increase of crystallinity. In summary, it was

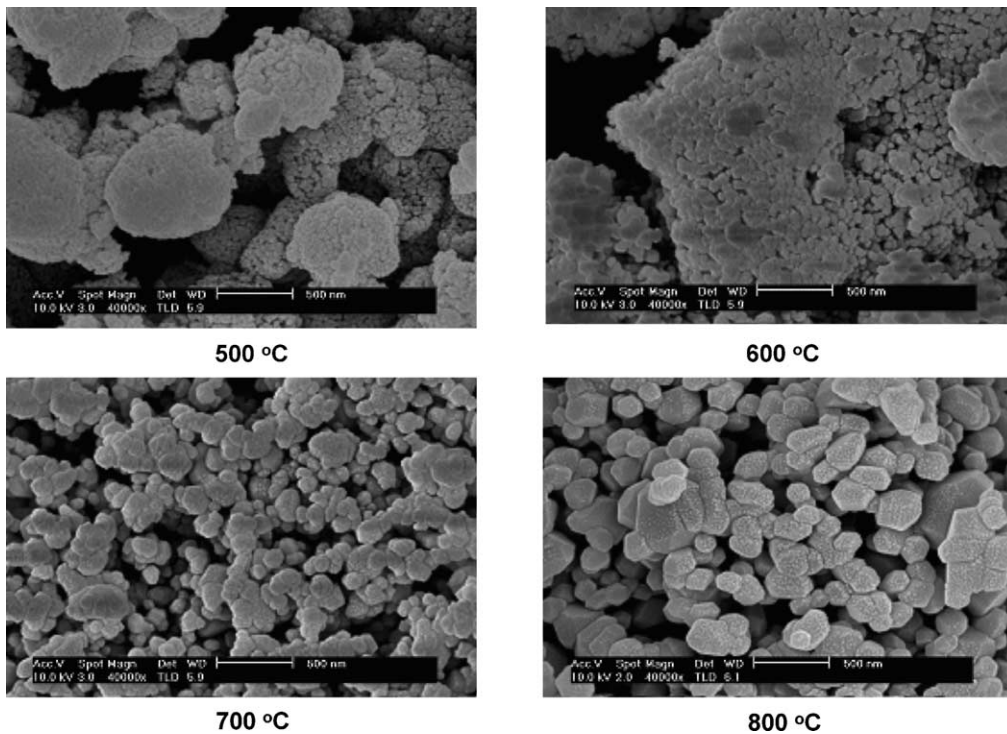


Fig. 2. SEM images of Co_3O_4 with respect to their synthetic temperatures.

observed that the electrochemical properties of Co_3O_4 are not related to its synthetic time, whereas the higher its synthetic temperature is, the better the electrochemical properties such as capacity and cycle life become. Thus, in our experiment, the optimum synthetic temperature for Co_3O_4 was fixed at 800°C , while its optimum synthetic time was arbitrarily positioned at 12 h.

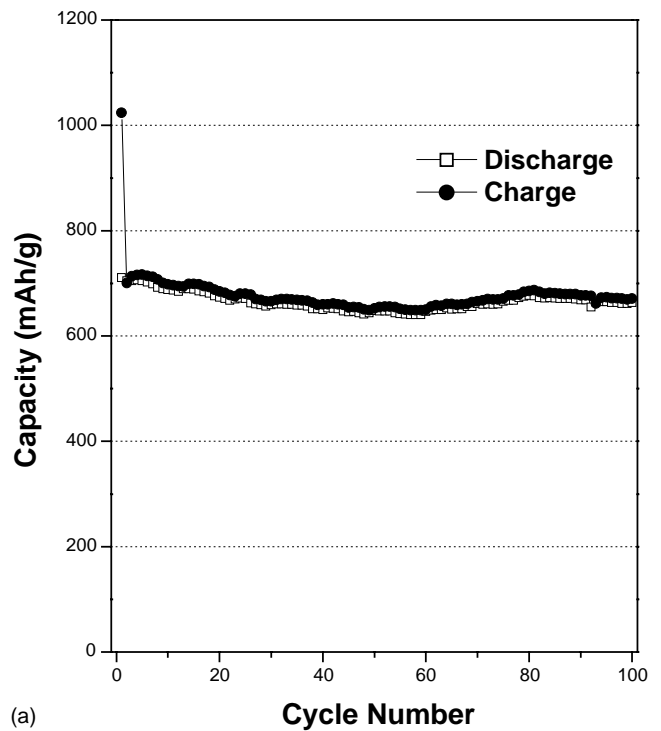
3.2. Several advantages and disadvantages in the electrochemical properties of Co_3O_4 as an anode material

Co_3O_4 prepared under optimum conditions showed promising electrochemical properties as an anode material for Li ion secondary batteries. As shown in Fig. 4, its capacity came to about 700 mAh/g, twice as high as graphite, and 93.4% of the initial capacity was maintained after 100 cycles. Even in the rate capability (Fig. 5), it showed a good property that the capacity at 1C reached about 90% of that at 0.2C. However, it can be confirmed also by Fig. 4 that Co_3O_4 showed too high discharge potential as an anode material and its initial coulombic efficiency was only 68.63%. Although the high discharge potential of Co_3O_4 reduces the operational potential and energy density of cell, where Co_3O_4 is used as the anode material, the cell with low voltage around 2–3 V is now prevailing for preventing the circuit short induced by high voltage. That is, high discharge potential of Co_3O_4 cannot be regarded as a disadvantage any more. On the other hand, the initial coulombic efficiency of Co_3O_4 is too low compared to that of the commercial anode material, graphite. Therefore, in order to substitute Co_3O_4 for graphite, its initial coulombic efficiency should be improved in the first place.

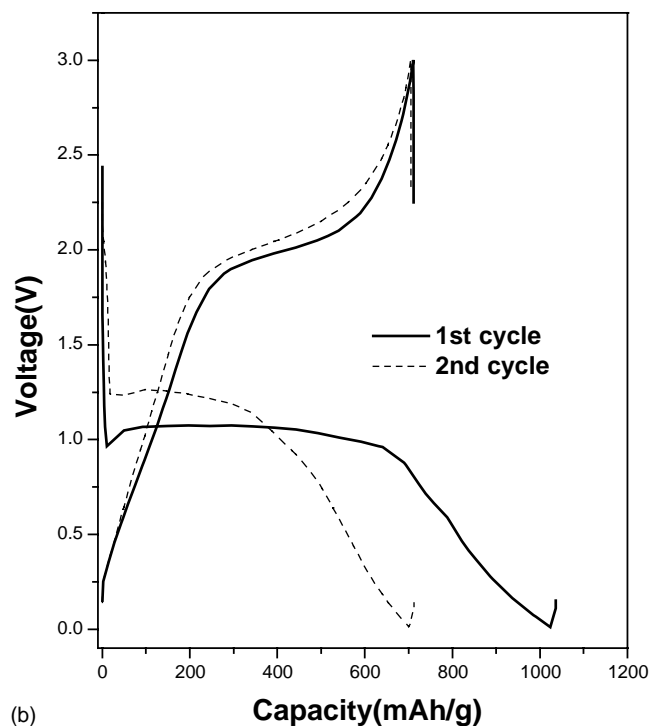
3.3. The methodologies for improving the initial coulombic efficiency of Co_3O_4 and their effects

Previous research for the transition material oxides reported that Co_3O_4 is charged and discharged by the formation and decomposition of Li_2O . Because Li_2O is an electrochemically inactive material [13,14], the incomplete decomposition of Li_2O during the first discharge has been surmised to be one of the main causes for the low initial coulombic efficiency of Co_3O_4 . In our previous work, this assumption was confirmed [10].

Ni is well known as one of elements that have the highest catalytic activity among transition metals. (This fact can be confirmed by Volcano curve.) Moreover, this material has been used as the catalyst for not only the reduction of H_2 or O_2 on the surface of single wall nanotubes [15] but also the decomposition of Li_2S that has a similar bond enthalpy to Li_2O (bond enthalpy of Li_2S : 312.5 kJ/mol, bond enthalpy of Li_2O : 333.5 kJ/mol). Therefore, the Ni addition to Li_2O was expected to make Li_2O easy to decompose. Because this hypothesis has not been proven until now, we endeavored to assure this by several types of experiments. The CV curve in Fig. 6 shows that when Ni was added to Li_2O , the



(a)



(b)

Fig. 4. (a) Cycle life and (b) charge–discharge curves of Co_3O_4 prepared under optimum condition.

oxidation peaks and reduction peaks of Li_2O surged in comparison with as prepared Li_2O . However, because it has not been elucidated what reaction correlates with oxidation or reduction peaks in the CV of Li_2O , XRD analyses were conducted at 1.75, 2, 2.25 and 2.5 V during the oxidation reac-

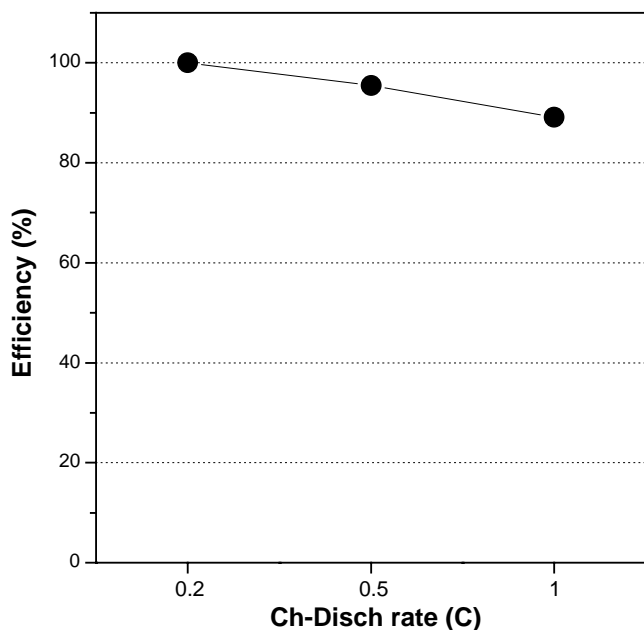


Fig. 5. Rate capability of Co_3O_4 ($1\text{C}/0.2\text{C} = 89.13\%$).

tion (Li ion extraction) as well as at 2.5, 1.8 and 1.25 V during the reduction reaction (Li ion insertion). From the XRD patterns in Fig. 7, it can be observed that while the Li ions are being extracted, the Li_2O peak continues to decrease.

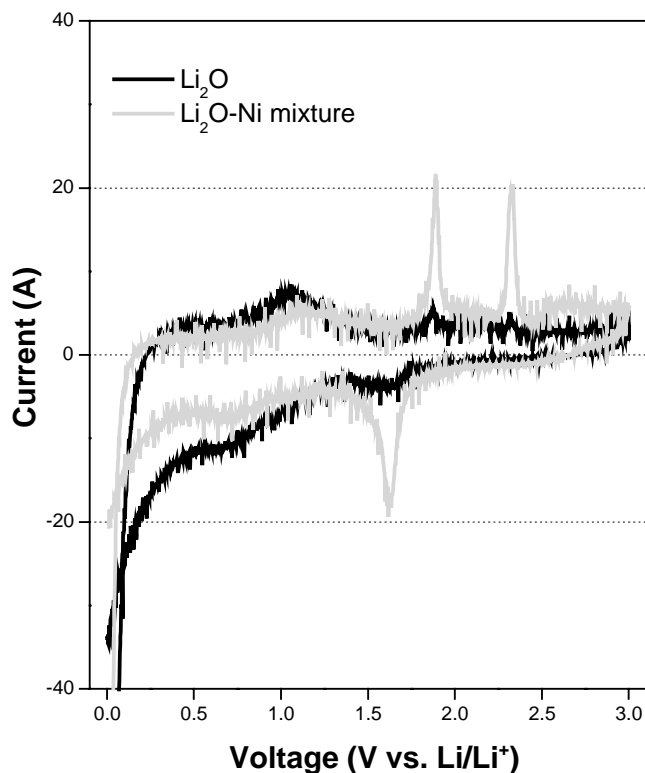


Fig. 6. Cyclic voltammograms of Li_2O (black color) and Ni added Li_2O (gray color). Addition of Ni enlarges the intensities of the oxidation peak and the reduction peak.

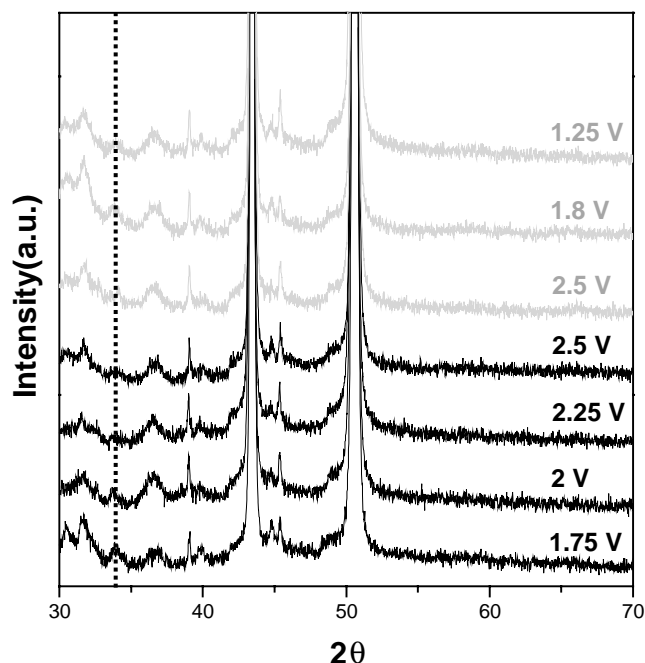


Fig. 7. XRD patterns for Li_2O at 1.75, 2, 2.25 and 2.5 V during the oxidation reaction (Li ion extraction, these figures have black color), and at 2.5, 1.8 and 1.25 V during the reduction reaction (Li ion insertion, these figures have gray color).

On the other hand, while the Li ions are being inserted, the Li_2O peak increases. From this result, it is easily confirmed that the oxidation peak and the reduction peak in the CV of Li_2O correspond to Li_2O decomposition and formation, respectively. Therefore, it can be assured that by adding Ni to Co_3O_4 , Li_2O decomposition is facilitated during the first discharge of Co_3O_4 .

First of all, mechanical milling was selected as a method to add Ni to Co_3O_4 . As shown in Fig. 8, Ni- Co_3O_4 composites prepared using mechanical milling showed variations in the electrochemical properties according to the mechanical milling time and the amount of Ni addition. Fig. 8a indicates that the higher the amount of Ni addition, the better the initial coulombic efficiency of Co_3O_4 . However, when the amount of Ni addition was over 10 wt.% of Co_3O_4 , the capacity of Co_3O_4 decreased drastically. Since Ni is an inactive material for Li ion, the increase of Ni in Ni- Co_3O_4 composite may well reduce its capacity. Hence, it may look bizarre that when the amount of Ni was varied from 0 to 10 wt.%, the capacity of Ni- Co_3O_4 composite was maintained. But, if it is considered that the initial coulombic efficiency of Ni- Co_3O_4 composite was much improved with the amount of Ni addition between 0 and 10 wt.%, we can assume that in spite of the decrease of charge capacity, the abrupt increase in the initial coulombic efficiency (discharge capacity to charge capacity) may restrain the loss of discharge capacity. Large capacity loss at Ni amount of 15 wt.% was caused by the enormous reduction of charge capacity. So, it is likely that this phenomenon is because the abundant Ni particles interfere with

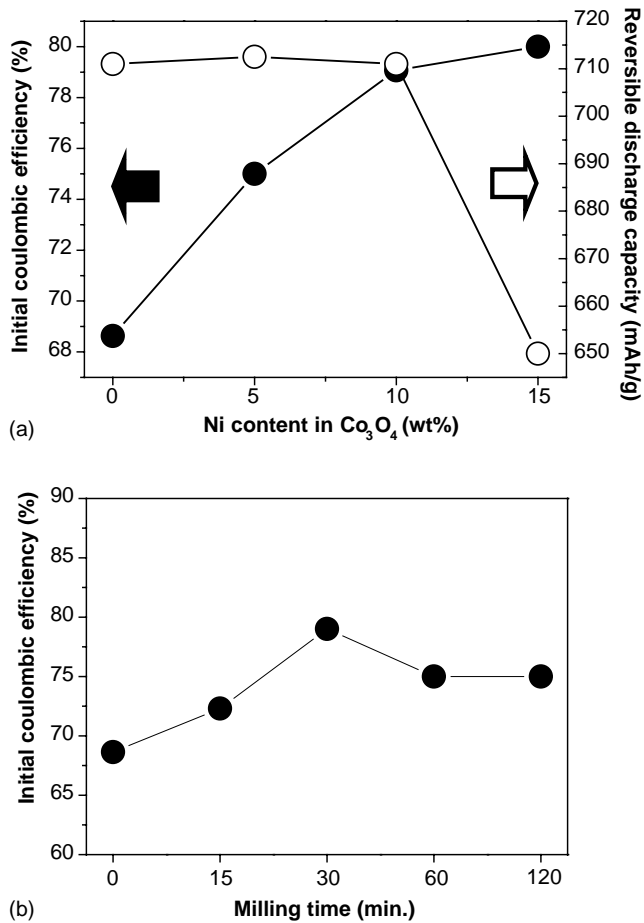


Fig. 8. (a) The changes in the reversible discharge capacity and the initial coulombic efficiency of Ni- Co_3O_4 composites as the function of Ni content. (b) The change in the initial coulombic efficiency of Ni- Co_3O_4 composite as the function of milling time.

Li ion insertion into Co_3O_4 . From Fig. 8b, it can be seen that Co_3O_4 mechanically milled with Ni for 30 min. had the best initial coulombic efficiency. Based on the previous result, the mechanical milling over 30 min. is thought to cause not only the homogeneous dispersion of Ni on Co_3O_4 but also the deterioration of structure in Co_3O_4 . Therefore, in our experiment, 30 min was fixed as the optimum mechanical milling time for the preparation of Ni- Co_3O_4 composite, while 10 wt.% was selected as the optimum amount of Ni addition. As a result, we could greatly improve the initial coulombic efficiency. As shown in Fig. 9, Ni- Co_3O_4 composite manufactured using mechanical milling under optimum conditions shows similar charge–discharge behaviors and capacity to Co_3O_4 , but its initial coulombic efficiency around 79% is much better than that of Co_3O_4 , 68.63%. On the other hand, when the mixture comprised of 10 wt.% Ni and 90 wt.% Co_3O_4 was made by physical mixing in a mortar, it showed the electrochemical behaviors differing from Ni- Co_3O_4 composite prepared by mechanical milling. As shown in Fig. 10, this mixture exhibited a little lower capacity than Co_3O_4 , and its initial coulombic efficiency was sim-

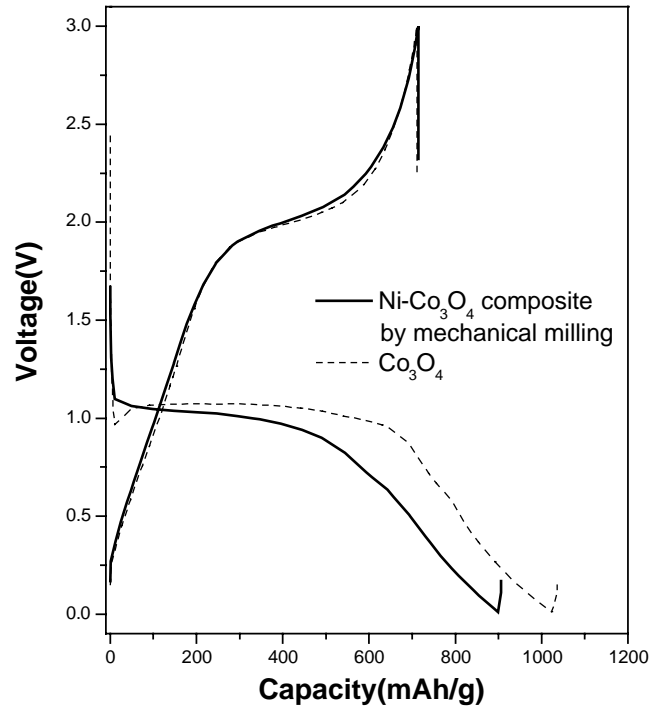


Fig. 9. The comparison between the initial charge–discharge curves of Co_3O_4 and Ni- Co_3O_4 composite prepared by mechanical milling.

ilar to that of Co_3O_4 . The SEM images in Fig. 11 may suggest the main reason for the difference between Ni- Co_3O_4 composite (Fig. 11a) and Ni- Co_3O_4 mixture (Fig. 11b). In this figure, none of Ni particles can be seen on the surface

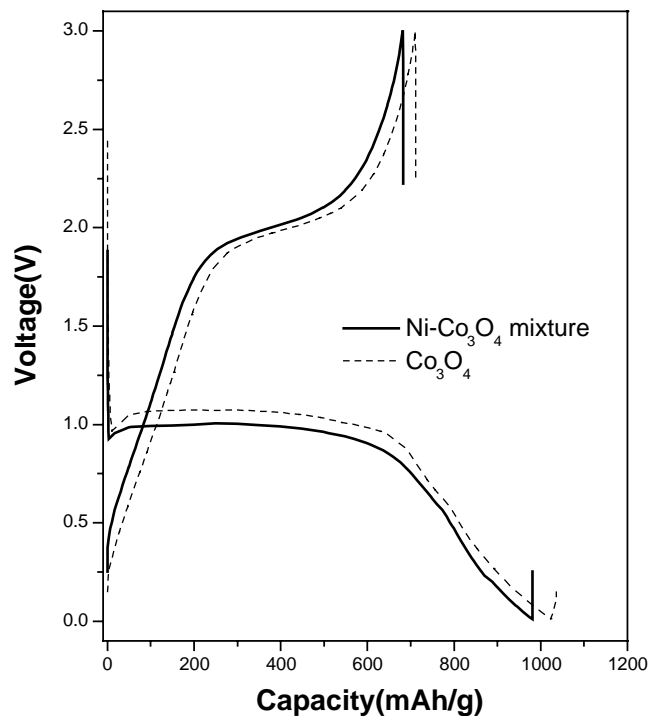
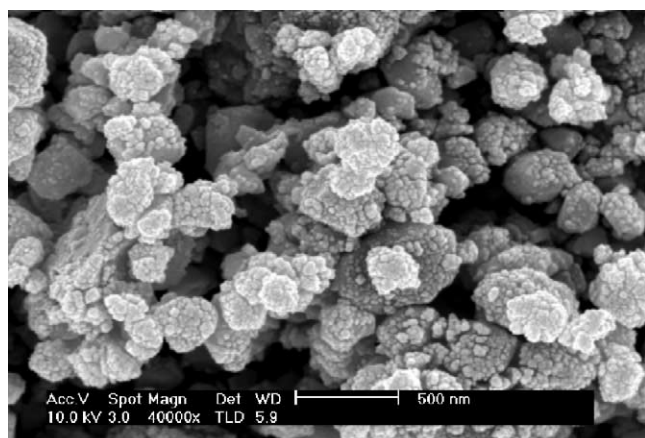
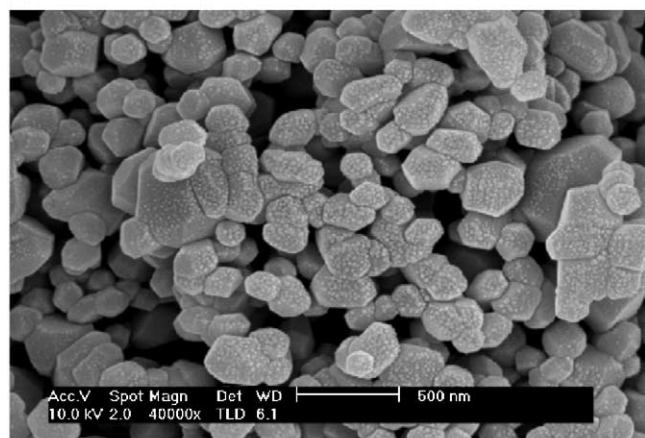


Fig. 10. The comparison between the initial charge–discharge curves of Co_3O_4 and Ni- Co_3O_4 mixture obtained by physical mixing in a mortar.



(a)



(b)

Fig. 11. SEM images of (a) Ni–Co₃O₄ composite prepared by mechanical milling and (b) Ni–Co₃O₄ mixture obtained by physical mixing in a mortar.

of Ni–Co₃O₄ mixture made by physical mixing in mortar, whereas the surface of Ni–Co₃O₄ composite made by the mechanical milling is fully covered with Ni particles. In order that Ni in Ni–Co₃O₄ composite may enable the irreversible portion of Li₂O to decompose during the 1st discharge, the contact area between Ni and Co₃O₄ should be enlarged as much as possible. Hence, it seems that there was a large disparity between mechanical milling and physical mixing in mortar in the contact area between Ni and Co₃O₄, which results from the homogeneity of Ni dispersion on Co₃O₄. When this morphological difference is considered, it can be thought that the initial coulombic efficiencies of Ni–Co₃O₄ mixture and Ni–Co₃O₄ composite are dependent on the contact area between Ni and Co₃O₄.

4. Conclusions

Under the optimized conditions, Co₃O₄ showed a high capacity around 700 mAh/g and stable capacity retention

during cycling (93.4% of initial capacity was retained after 100 cycles). However, its initial coulombic efficiency was only about 69%. Several phenomenological examinations in our previous results informed us that one of the main reasons for the low initial coulombic efficiency of Co₃O₄ was the incomplete decomposition of Li₂O during the first discharge. In previous reports, it was assumed that a transition metal like Ni has the catalytic activity to facilitate Li₂O decomposition. Up to now, this premise had not been proven by any work. However, since CV and XRD results in this work showed that Ni addition to Li₂O amplifies the decomposition and reduction of Li₂O, Ni addition was chosen as the method to improve the initial coulombic efficiency of Co₃O₄. Mechanical milling was used to add Ni to Co₃O₄. The charge–discharge tests with Ni–Co₃O₄ composites obtained under various preparation conditions indicated that 10 wt.% of Co₃O₄ was the optimum amount of Ni addition and 30 min. was the optimum milling time. Ni–Co₃O₄ composite prepared by mechanical milling under these optimum conditions showed much improved initial coulombic efficiency around 79%. In addition, when Ni–Co₃O₄ mixture was manufactured by physical mixing in a mortar, its initial coulombic efficiency was nearly the same as that of Co₃O₄. Based on the morphologies of these materials, it was determined that the degree of improvement in the initial coulombic efficiency of Ni–Co₃O₄ composite or mixture is proportional to the homogeneity of Ni dispersion on Co₃O₄. Consequently, it can be surmised that the initial coulombic efficiency of Ni–Co₃O₄ composite mainly depends on the contact area between Ni and Co₃O₄.

Acknowledgements

The authors wish to express thanks to the LG Chemical Ltd., Research Park, IREX, Australian Research Council (ARC) linkage project for its partial financial support of this work and Dr. T. Silver for careful reading of the manuscript and valuable remarks.

References

- [1] K. Sekai, H. Azuma, A. Omaru, S. Fujita, H. Imoto, T. Endo, K. Yamaura, Y. Nishi, S. Mashiko, M. Yokogawa, J. Power Sources 43–44 (1993) 241.
- [2] J.R. Dahn, U.V. Sacken, C.A. Michal, Solid State Ionics 44 (1990) 87.
- [3] T. Ohzuku, M. Kitagawa, T. Hirai, J. Electrochem. Soc. 137 (1990) 769.
- [4] A. Yamada, M. Hosoya, S.C. Chung, Y. Kudo, K. Hinokuma, K.Y. Liu, Y. Nishi, J. Power Sources 119–121 (2003) 232.
- [5] K. Sawai, Y. Iwakoshi, T. Ohzuku, Solid State Ionics 69 (1994) 273.
- [6] J.R. Dahn, A.K. Sleight, H. Shi, J.N. Reimers, O. Zhong, B.M. Way, Electrochim. Acta 38 (1993) 1179.
- [7] R. Yazami, D. Guerard, J. Power Sources 43–44 (1993) 39.

- [8] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.M. Tarascon, *Nature* 407 (2000) 496.
- [9] D. Larcher, G. Sudant, J.B. Leriche, Y. Chabre, J.M. Tarascon, *J. Electrochem. Soc.* 149 (2002) A234.
- [10] Y.M. Kang, K.T. Kim, K.Y. Lee, S.J. Lee, J.H. Jung, J.Y. Lee, *J. Electrochem. Soc.* 150 (2003) A1538.
- [11] H. Li, L. Shi, Q. Wang, L. Chen, X. Huang, *Solids State Ionics* 148 (2002) 247.
- [12] S. Grugeon, S. Laruelle, R. Herrera-Urbina, L. Dupont, P. Poizot, J.M. Tarascon, *J. Electrochem. Soc.* 148 (2001) A285.
- [13] Y. Idota, T. Kubota, A. Matsufuji, Y. Maekawa, T. Miyasaka, *Science* 276 (1997) 1395.
- [14] K. Wan, S.F.Y. Li, Z. Gao, K.S. Siow, *J. Power Sources* 75 (1998) 9.
- [15] R.I. Masel, *Principles of Adsorption and Reaction on Solid Surfaces*, Wiley, 1996.