

University of Wollongong

Research Online

Australian Institute for Innovative Materials -
Papers

Australian Institute for Innovative Materials

2005

A study on the charge-discharge mechanism of Co₃O₄ as an anode for the Li ion secondary battery

Yong-Mook Kang

Korea Advanced Institute of Science and Technology, South Korea

Min-Sang Song

Korea Advanced Institute of Science and Technology, South Korea

Jin-Ho Kim

Korea Advanced Institute of Science and Technology, South Korea

Hyun-Seok Kim

Korea Advanced Institute of Science and Technology, South Korea

Min-Sik Park

Korea Advanced Institute of Science and Technology, South Korea, msp532@uow.edu.au

See next page for additional authors

Follow this and additional works at: <https://ro.uow.edu.au/aiimpapers>



Part of the [Engineering Commons](#), and the [Physical Sciences and Mathematics Commons](#)

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

A study on the charge-discharge mechanism of Co₃O₄ as an anode for the Li ion secondary battery

Abstract

Co₃O₄ has shown acceptable electrochemical properties as the anode material of Li secondary batteries. In detail, its capacity reached about 700 mAh/g, twice as high as graphite, and 93.4% of initial capacity was retained after 100 cycles. EIS (electrochemical impedance spectroscopy) analyses revealed that after the 1st cycle, the insertion or extraction of Li ions in Co₃O₄ can occur homogeneously and reversibly (randless-like behavior, homogeneous mixture: Co + Li₂O (in the state of Li insertion), Co₃O₄ (in the state of Li extraction)). In fact, the coulombic efficiency of Co₃O₄ was almost 100% except for the 1st cycle. According to P. Poizot's research on several kinds of transition metal oxides, such as Co₃O₄, CoO, NiO, etc., a small Li₂O particle size and catalytic activity of the transition metal are expected to decrease the binding energy of Li₂O tremendously. As a result, Li₂O should be easy to decompose, and transition metal oxides should be able to charge or discharge reversibly by formation or decomposition of Li₂O. However, this assumption has never been confirmed by experimental results. In our results, the CV (cyclic voltammogram) of a Li₂O–Co mixture shows much larger oxidation and reduction peaks than that of Li₂O. Based on XRD analyses, oxidation and reduction in the CV of Li₂O correspond, respectively, to the decomposition and formation of Li₂O. So, it can be asserted that Co addition to Li₂O facilitates decomposition and formation processes in Li₂O and that the catalytic effect of the transition metal must be one of the main causes that make Li₂O form or decompose repeatedly.

Keywords

study, charge, discharge, mechanism, Co₃O₄, anode, for, ion, secondary, battery

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Kang, Y, Song, M, Kim, J, Kim, H, Park, M, Lee, J, Liu, HK, & Dou, SX (2005), A study on the charge-discharge mechanism of Co₃O₄ as an anode for the Li ion secondary battery, *Electrochimica Acta*, 50, pp. 3667-3673.

Authors

Yong-Mook Kang, Min-Sang Song, Jin-Ho Kim, Hyun-Seok Kim, Min-Sik Park, Jai-Young Lee, Hua-Kun Liu, and S X. Dou

A study on the charge–discharge mechanism of Co_3O_4 as an anode for the Li ion secondary battery

Yong-Mook Kang^{a,*}, Min-Sang Song^a, Jin-Ho Kim^a,
Hyun-Seok Kim^a, Min-Sik Park^a, Jai-Young Lee^a, H.K. Liu^b, S.X. Dou^b

^a Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology,

373-1 Guseong-Dong, Yuseong-gu, Daejeon 305701, South Korea

^b ISEM, University of Wollongong, Wollongong, 2522 NSW, Australia

Received 12 July 2004; received in revised form 9 January 2005; accepted 13 January 2005

Available online 17 February 2005

Abstract

Co_3O_4 has shown acceptable electrochemical properties as the anode material of Li secondary batteries. In detail, its capacity reached about 700 mAh/g, twice as high as graphite, and 93.4% of initial capacity was retained after 100 cycles. EIS (electrochemical impedance spectroscopy) analyses revealed that after the 1st cycle, the insertion or extraction of Li ions in Co_3O_4 can occur homogeneously and reversibly (randless-like behavior, homogeneous mixture: $\text{Co} + \text{Li}_2\text{O}$ (in the state of Li insertion), Co_3O_4 (in the state of Li extraction)). In fact, the coulombic efficiency of Co_3O_4 was almost 100% except for the 1st cycle. According to P. Poizot's research on several kinds of transition metal oxides, such as Co_3O_4 , CoO , NiO , etc., a small Li_2O particle size and catalytic activity of the transition metal are expected to decrease the binding energy of Li_2O tremendously. As a result, Li_2O should be easy to decompose, and transition metal oxides should be able to charge or discharge reversibly by formation or decomposition of Li_2O . However, this assumption has never been confirmed by experimental results. In our results, the CV (cyclic voltammogram) of a Li_2O –Co mixture shows much larger oxidation and reduction peaks than that of Li_2O . Based on XRD analyses, oxidation and reduction in the CV of Li_2O correspond, respectively, to the decomposition and formation of Li_2O . So, it can be asserted that Co addition to Li_2O facilitates decomposition and formation processes in Li_2O and that the catalytic effect of the transition metal must be one of the main causes that make Li_2O form or decompose repeatedly.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Li ion battery; Anode; The catalytic effect of Co; Charge–discharge mechanism; Transition metal oxides

1. Introduction

Lithium ion insertion materials have received considerable attention because they can be used as an active electrode in Li ion secondary batteries, which have potential applications ranging from portable electronic devices to electric vehicles. Negative electrodes in the small commercial rechargeable lithium-based batteries that are currently available typically employ solid solutions of lithium in one or another form of carbon. However, with the growing demand for high capacity secondary batteries, the low capacity of carbon (theoretical

capacity: 372 mAh/g) has become a limiting factor in wider applications [1–3], and high capacity alternatives to carbonaceous material have thus been sought for. Several materials, such as Sn alloys [4,5], Si composites [6], Li metal [7,8], oxides [9–11], and so on, have been testified as high capacity anode materials which can substitute for graphite. Because elements like Sn and Si can alloy and dealloy with Li reversibly and show low operating potential when used as the electrode material, they are reasonably adequate as anodes for Li ion secondary batteries [12]. However, they have been reported to suffer an enormous volume expansion during Li ion insertion, which results in their poor cyclic properties [13]. As the primary method for suppressing this change, it was proposed that material which could act as a buffer against

* Corresponding author. Tel.: +82 428693353; fax: +82 428698910.

E-mail address: dake@kaist.ac.kr (Y.-M. Kang).

volume expansion should be added [4,14]. In the first attempt, Sn alloys (SnCu, SnFe, etc.) and SnO were used as anodes of Li ion batteries to improve the cyclic property of Sn, but none of them showed any satisfactory cycle life. In order to overcome the limited cyclic property of Si, Si–C composite manufactured by CVD (chemical vapor deposition) [15] or by a ball milling process [16] was tried as the anode material. Si–C composite shows quite a good cyclic property, but because the quantity of Si that can react with Li ions in Si–C composite is much lower than in Si, its capacity is not much improved compared to the commercial anode material (graphite). Li metal also has a very high capacity (3860 and 2060 mAh/cm³). Because the formation of dendrites on the surface of Li metal during charging–discharging induces a drastic degradation of the cyclic property, it is not suitable for use as an anode material without the development of a special electrolyte [7].

Since Li ion batteries were generalized as the commercial rechargeable battery, LiCoO₂ [17] has been utilized as the cathode material and other kinds of transition metal oxides, such as LiNiO₂ [18], LiMn₂O₄ [19] and recently, LiFePO₄ [20] were tried as substitutes for LiCoO₂. 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 the anode material for Li ion batteries. From then on, transition metal oxides have received much attention not only as cathode materials but also as anode materials. When transition metal oxides, such as Co₃O₄, CoO, NiO, FeO, etc., are used as the anode material, their charge–discharge mechanism is definitely different from that of transition metal oxides like LiCoO₂ and LiMn₂O₄, which are known as cathode materials. Whatever transition metal oxides used as cathode materials have for their structure, they are reported to charge or discharge by Li ion intercalation or deintercalation. On the other hand, based on previous research, the formation and decomposition of Li₂O have been presented as the charge–discharge mechanism of transition metal oxides for anodes [11,21]. Although many researchers, such as J.M. Tarascon have insisted that in transition metal oxides, Li₂O formation or decomposition is basically reversible, many works attribute large irreversible capacity of SnO [22], TCO [4], etc., to Li₂O. Among several kinds of transition metal oxides, CoO and Co₃O₄ show good cycle life as well as high capacity. Just like the other transition metal oxides, CoO [11,21] and Co₃O₄ [23] seem to be charged or discharged by formation or decomposition of Li₂O. However, because Li₂O is well known as a stable material, it would be irreversible as the electrode material in a charge or discharge process. (For example, the main cause of large irreversible capacity in SnO is due to the formation of Li₂O at the 1st charge reaction [4,22].) Poizot et al. [11,21] surmised that the reversible formation and decomposition of Li₂O on transition metal oxides, such as Co₃O₄ and CoO result from the precipitously reduced binding energy of Li₂O,

which is due to the small particle size of Li₂O and the catalytic activity of the transition metal. Though this assumption has been quoted by other researchers, it has not been proved by any experimental work. Hence, in this paper, we report that Co₃O₄ can be charged or discharged by formation or decomposition of Li₂O. Finally, several experimental works will be given to know why Li₂O, that is known as a representative irreversible material is able to form and decompose reversibly.

2. Experimental procedures

CoCO₃ was used as a precursor in this experiment. The CoCO₃ was heated at 800 °C for 12 h in air, to yield Co oxide. The quantitative composition of Co oxide obtained from this process was confirmed by the XRD (X-ray diffraction) pattern.

In order to fabricate Co oxide electrodes, Co oxide powder was mixed with acetylene black as a conductive agent and polyvinylidene fluoride (PVDF) as a binder in a mass ratio of 72:20:8. Co oxide and acetylene black powders were first added to a solution of PVDF in *N*-methyl-2-pyrrolidinone (NMP) to make the slurry with appropriate viscosity. Cu mesh was then used to coat the mixture. 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. Coin-type cells were used for the charging–discharging experiment, and this experiment was not a full cell test but a half cell test. (Differing from the full cell in which Co₃O₄ electrode plays a role of the negative electrode (anode), Li ion insertion and extraction in Co₃O₄ are related to the discharge and charge process, respectively. However, note that the charge and discharge process of Co₃O₄ electrodes are named according to the full cell test where the Co₃O₄ electrode acts as the negative electrode.) Therefore, coin cells were assembled in an argon filled glove box, where the counter electrode was Li metal and the electrolyte was 1 M LiPF₆ dissolved in a 50/50 vol.% mixture of ethylene carbonate (EC) and diethyl carbonate (DEC).

The anode performance of the Co₃O₄ samples was measured in the 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). In order to analyze the electrochemical impedance response, a Solatron 1255 frequency response analyzer (FRA) was used in conjunction with the Solatron 1286 electrochemical interface. After the electrode reached an equilibrium potential, the electrochemical impedance measurements were carried out by applying an ac voltage of 5 mV over the frequency range from 1 to 100 kHz. To measure the reversibility in formation or decomposition of Li₂O, cyclic voltammograms (CV) were obtained for Li₂O and the mixture of Li₂O–Co, which was prepared by ball milling Li₂O (50 μm) and Co (10 μm) at the ratio of 90 wt. %:10 wt. %.

XRD examination was performed using monochromatic Cu Kα radiation to observe the crystallinity of Co oxide as

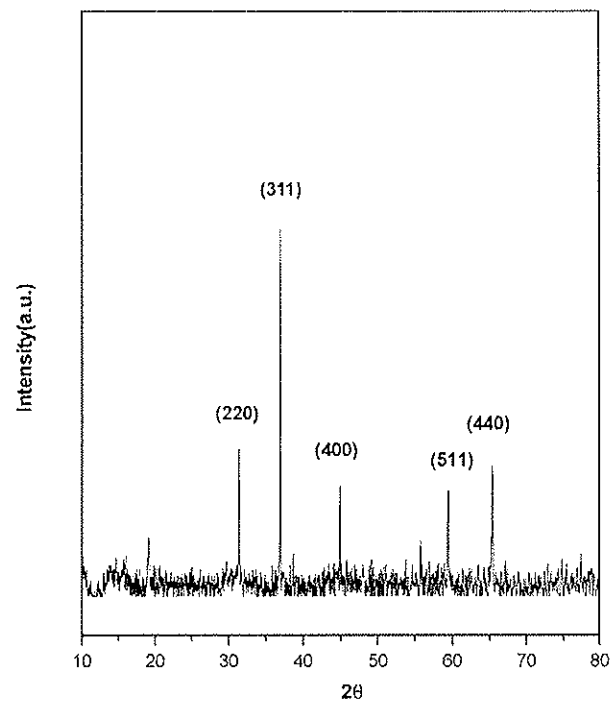


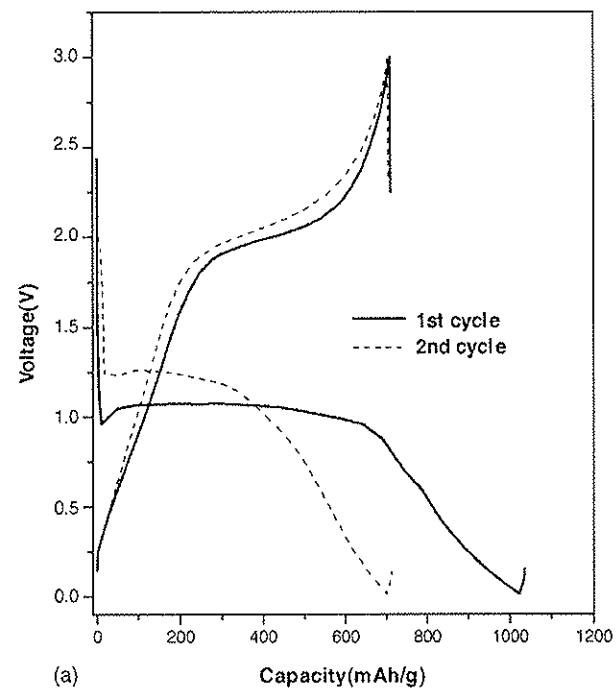
Fig. 1. XRD pattern of Co oxide obtained from the solid-state reaction of CoCO_3 in air. Co oxide was indexed as Co_3O_4 .

well as the change of Li_2O during the oxidation or reduction. After cycling, 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 . When the dried electrodes were subjected to TEM (transmission electron microscopy), the phase transition of Co_3O_4 during cycling was confirmed.

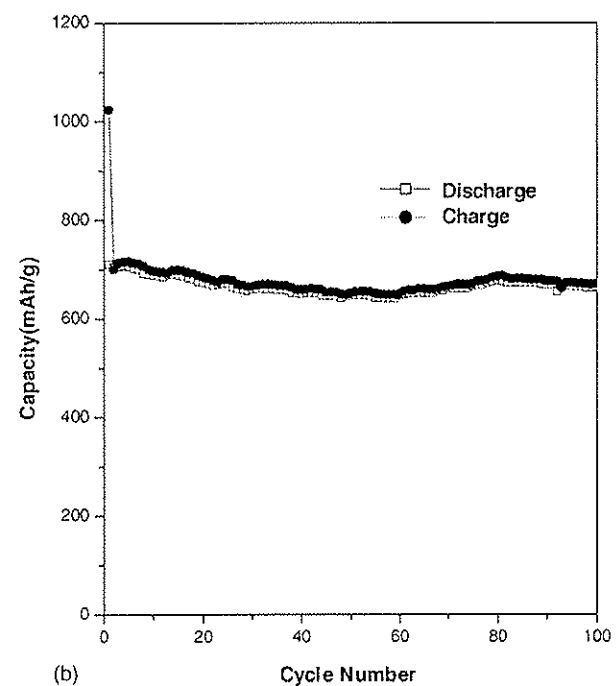
3. Results and discussion

3.1. General properties of Co_3O_4 as an anode material and the reason why the charge–discharge mechanism of transition metal oxides, such as Co_3O_4 should be clarified

In the current study, Co oxide was manufactured from the solid-state reaction of CoCO_3 in air. The XRD pattern of Co oxide (Fig. 1) prepared from this reaction shows that this product corresponds to Co_3O_4 . When Co_3O_4 is charged and discharged between 0.01 and 3.0 V, as shown in Fig. 2(a), Co_3O_4 has enough low potential to be used as an anode material for Li ion batteries and much higher capacity than graphite, the commercial anode material. Furthermore, it can be seen from Fig. 2(b) that except for the 1st cycle, Co_3O_4 retains good coulombic efficiency at every cycle, which leads to an outstanding cycle life, with 93.4% of initial capacity maintained after 100 cycles. However, in order to confirm



(a)



(b)

Fig. 2. (a) Charge–discharge curves and (b) cycle life of Co_3O_4 obtained from the solid-state reaction at 800°C .

whether Co_3O_4 can be charged and discharged by reversible formation and decomposition of Li_2O , it should be verified why the formation and decomposition of Li_2O are reversible during the charge and discharge of Co_3O_4 . The reason of large initial irreversible capacity observed in Fig. 2(b) can be confirmed in our previous paper [24].

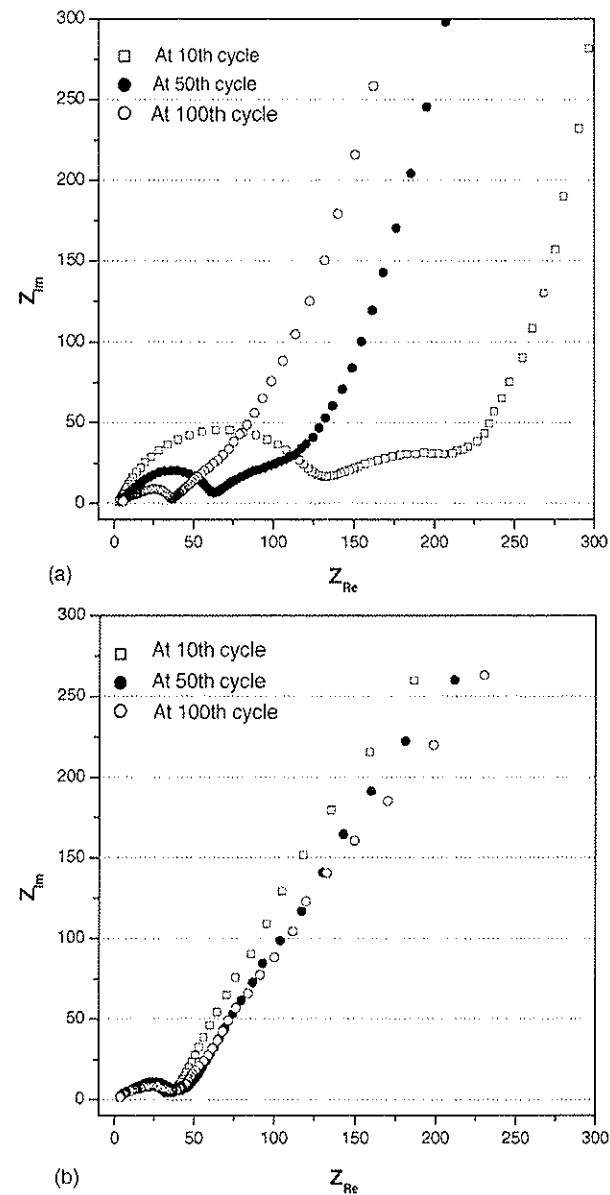


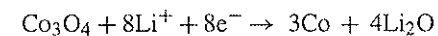
Fig. 3. Nyquist plots of Co_3O_4 's (a) in the charged state (0.01 V) and (b) in the discharged state (1.2 V) at the 10th, 50th, and 100th cycle (randless-like behavior).

3.2. Reversible charge–discharge mechanism of Co_3O_4

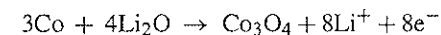
For elucidating the reason why Li_2O can be reversibly formed or decomposed, above all, EIS analyses were conducted for Co_3O_4 at the 10th, 50th, and 100th cycle (Fig. 3). Fig. 3(a) shows that in the Li inserted state (that is to say, 0.01 V) of Co_3O_4 at every cycle, there are two semicircles related to some kind of resistance. In case of oxide materials, the 1st semicircle at higher frequency is related to the formation of passivation film on the surface and the 2nd semicircle at lower frequency is related to the Li absorption/desorption process, that is, charge transfer at interface.

As shown in Fig. 3(a), the 2nd semicircle (charge-transfer resistance at the interface) is drastically restrained as the cycle number increases, and after all, it disappears at 100th cycle. This phenomenon is because the interface between passivation film and material, which is activated by formation or decomposition of Co_3O_4 or the mixture of Li_2O and Co at the previous cycles, can not obstruct Li ion transfer any more at 100th cycle [25]. During Li extraction (in other words, when the potential of electrode changes from 0.01 to 1.2 V), there is just one small semicircle and one Warburg impedance. Based on Macdonald [25], this phenomenon is called randless-like behavior and when this phenomenon occurs, whatever the charge–discharge mechanism of the electrode material is, it can be reversibly charged or discharged in homogeneous phases. Hence, we can think that Co_3O_4 is also able to charge or discharge in homogeneous phases. When SADP's (selected area diffraction patterns) were obtained in the Li inserted or Li extracted state at the 100th cycle, the images are shown in Fig. 4. From Fig. 4(a) and (b), it can be observed that SADP for as prepared Co_3O_4 shows the obvious crystalline pattern having $[\bar{1}13]$ as the zone axis, whereas in the Li inserted state at the 100th cycle, SADP is made up of several polycrystalline patterns (\blacktriangledown) and hollow rings (∇). As a result of indexing, it was revealed that the polycrystalline patterns correspond to Co nano-particles and the hollow rings occur due to Li_2O amorphous phase. On the other hand, Fig. 4(c) shows that in the Li extracted state at the 100th cycle, there are only several conspicuous polycrystalline patterns (\blacktriangledown), which were found by the subsequent indexing to correspond to Co_3O_4 . Therefore, it can be assumed that the homogeneous phases during Li insertion are a mixture of Li_2O amorphous phases and Co nano-particles, and during Li extraction, Co oxides can be expected as the possible homogeneous phases. Based on these results, the reversible reaction of Co_3O_4 can be expressed by this reaction connected to the formation or decomposition of Li_2O .

Li insertion process :



Li extraction process :



3.3. The main reason why Li_2O can be reversibly formed and decomposed during charging and discharging of Co_3O_4

In the previous section, it was shown that although Li_2O is a representative electrochemically irreversible material, Co_3O_4 is able to charge and discharge by the formation and decomposition of Li_2O . As for the reason why the reversible formation and decomposition of Li_2O are possible during charging and discharging of Co_3O_4 , Poizot et al. suggested that the reversible formation and decomposition of Li_2O re-

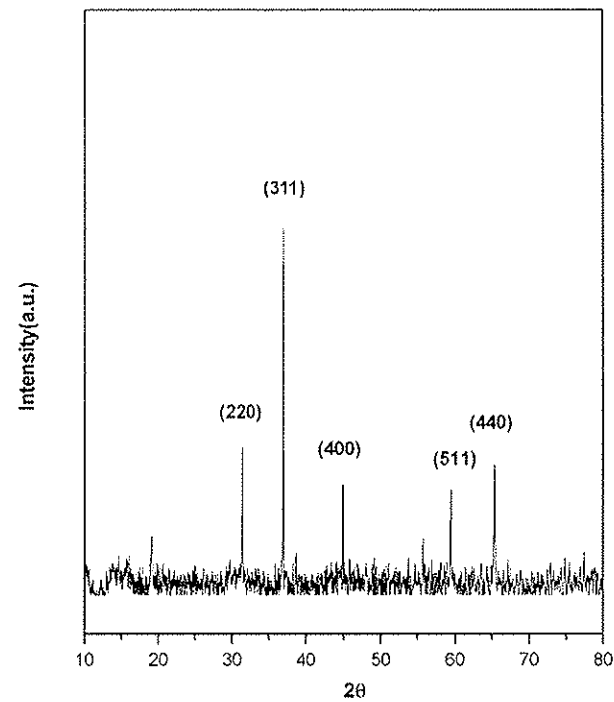


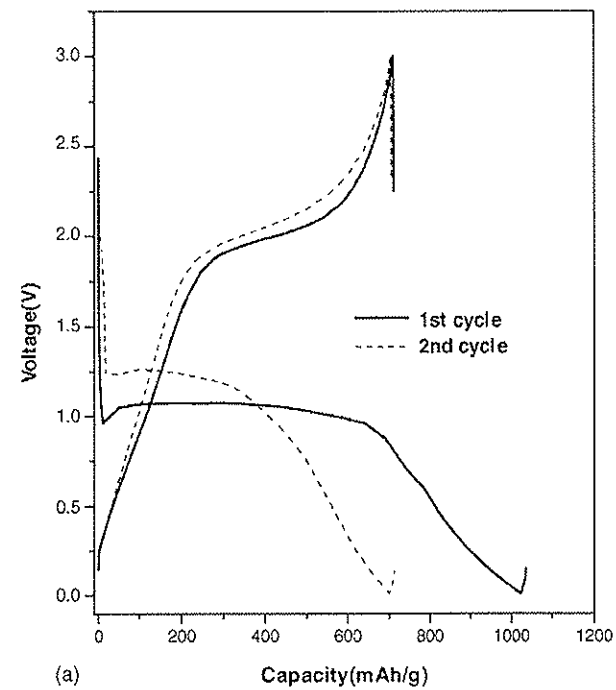
Fig. 1. XRD pattern of Co oxide obtained from the solid-state reaction of CoCO_3 in air. Co oxide was indexed as Co_3O_4 .

well as the change of Li_2O during the oxidation or reduction. After cycling, 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 . When the dried electrodes were subjected to TEM (transmission electron microscopy), the phase transition of Co_3O_4 during cycling was confirmed.

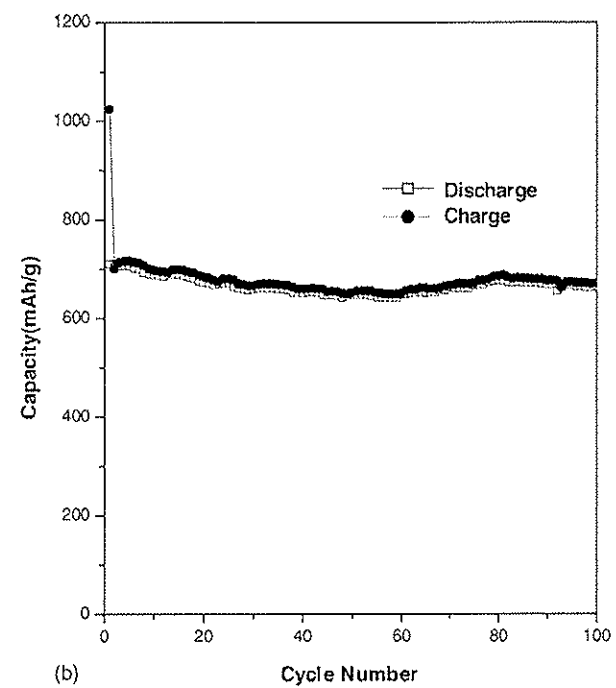
3. Results and discussion

3.1. General properties of Co_3O_4 as an anode material and the reason why the charge–discharge mechanism of transition metal oxides, such as Co_3O_4 should be clarified

In the current study, Co oxide was manufactured from the solid-state reaction of CoCO_3 in air. The XRD pattern of Co oxide (Fig. 1) prepared from this reaction shows that this product corresponds to Co_3O_4 . When Co_3O_4 is charged and discharged between 0.01 and 3.0 V, as shown in Fig. 2(a), Co_3O_4 has enough low potential to be used as an anode material for Li ion batteries and much higher capacity than graphite, the commercial anode material. Furthermore, it can be seen from Fig. 2(b) that except for the 1st cycle, Co_3O_4 retains good coulombic efficiency at every cycle, which leads to an outstanding cycle life, with 93.4% of initial capacity maintained after 100 cycles. However, in order to confirm



(a)



(b)

Fig. 2. (a) Charge–discharge curves and (b) cycle life of Co_3O_4 obtained from the solid-state reaction at 800°C .

whether Co_3O_4 can be charged and discharged by reversible formation and decomposition of Li_2O , it should be verified why the formation and decomposition of Li_2O are reversible during the charge and discharge of Co_3O_4 . The reason of large initial irreversible capacity observed in Fig. 2(b) can be confirmed in our previous paper [24].

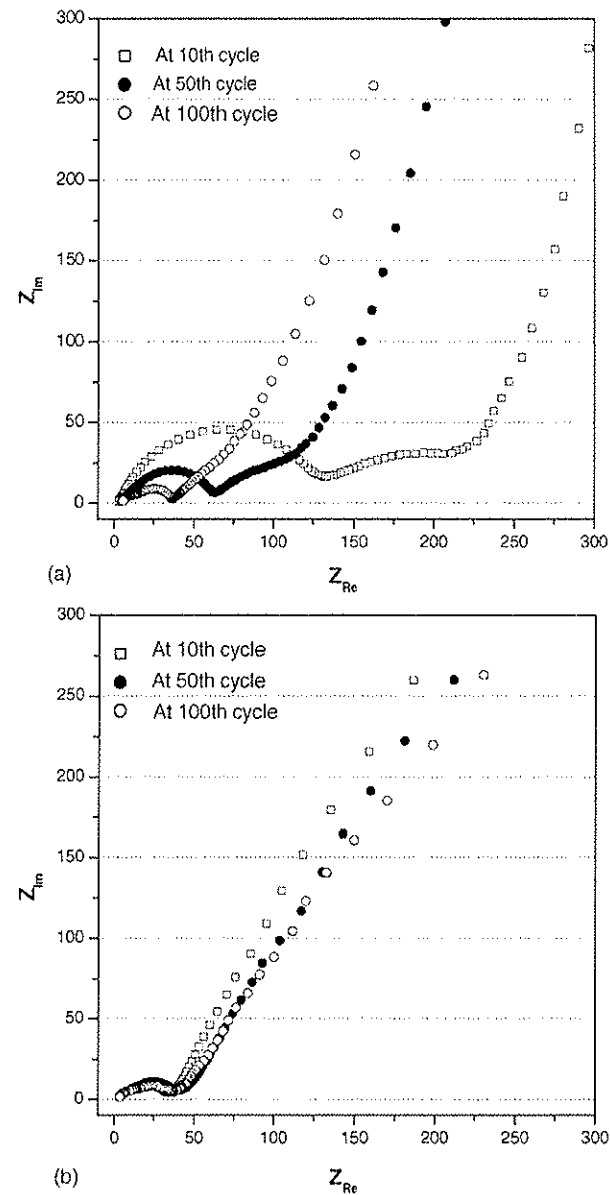


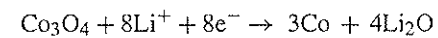
Fig. 3. Nyquist plots of Co_3O_4 's (a) in the charged state (0.01 V) and (b) in the discharged state (1.2 V) at the 10th, 50th, and 100th cycle (randless-like behavior).

3.2. Reversible charge–discharge mechanism of Co_3O_4

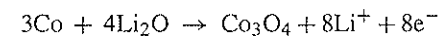
For elucidating the reason why Li_2O can be reversibly formed or decomposed, above all, EIS analyses were conducted for Co_3O_4 at the 10th, 50th, and 100th cycle (Fig. 3). Fig. 3(a) shows that in the Li inserted state (that is to say, 0.01 V) of Co_3O_4 at every cycle, there are two semicircles related to some kind of resistance. In case of oxide materials, the 1st semicircle at higher frequency is related to the formation of passivation film on the surface and the 2nd semicircle at lower frequency is related to the Li absorption/desorption process, that is, charge transfer at interface.

As shown in Fig. 3(a), the 2nd semicircle (charge-transfer resistance at the interface) is drastically restrained as the cycle number increases, and after all, it disappears at 100th cycle. This phenomenon is because the interface between passivation film and material, which is activated by formation or decomposition of Co_3O_4 or the mixture of Li_2O and Co at the previous cycles, can not obstruct Li ion transfer any more at 100th cycle [25]. During Li extraction (in other words, when the potential of electrode changes from 0.01 to 1.2 V), there is just one small semicircle and one Warburg impedance. Based on Macdonald [25], this phenomenon is called randless-like behavior and when this phenomenon occurs, whatever the charge–discharge mechanism of the electrode material is, it can be reversibly charged or discharged in homogeneous phases. Hence, we can think that Co_3O_4 is also able to charge or discharge in homogeneous phases. When SADP's (selected area diffraction patterns) were obtained in the Li inserted or Li extracted state at the 100th cycle, the images are shown in Fig. 4. From Fig. 4(a) and (b), it can be observed that SADP for as prepared Co_3O_4 shows the obvious crystalline pattern having $[\bar{1}13]$ as the zone axis, whereas in the Li inserted state at the 100th cycle, SADP is made up of several polycrystalline patterns (\blacktriangledown) and hollow rings (∇). As a result of indexing, it was revealed that the polycrystalline patterns correspond to Co nano-particles and the hollow rings occur due to Li_2O amorphous phase. On the other hand, Fig. 4(c) shows that in the Li extracted state at the 100th cycle, there are only several conspicuous polycrystalline patterns (\blacktriangledown), which were found by the subsequent indexing to correspond to Co_3O_4 . Therefore, it can be assumed that the homogeneous phases during Li insertion are a mixture of Li_2O amorphous phases and Co nano-particles, and during Li extraction, Co oxides can be expected as the possible homogeneous phases. Based on these results, the reversible reaction of Co_3O_4 can be expressed by this reaction connected to the formation or decomposition of Li_2O .

Li insertion process :



Li extraction process :



3.3. The main reason why Li_2O can be reversibly formed and decomposed during charging and discharging of Co_3O_4

In the previous section, it was shown that although Li_2O is a representative electrochemically irreversible material, Co_3O_4 is able to charge and discharge by the formation and decomposition of Li_2O . As for the reason why the reversible formation and decomposition of Li_2O are possible during charging and discharging of Co_3O_4 , Poizot et al. suggested that the reversible formation and decomposition of Li_2O re-

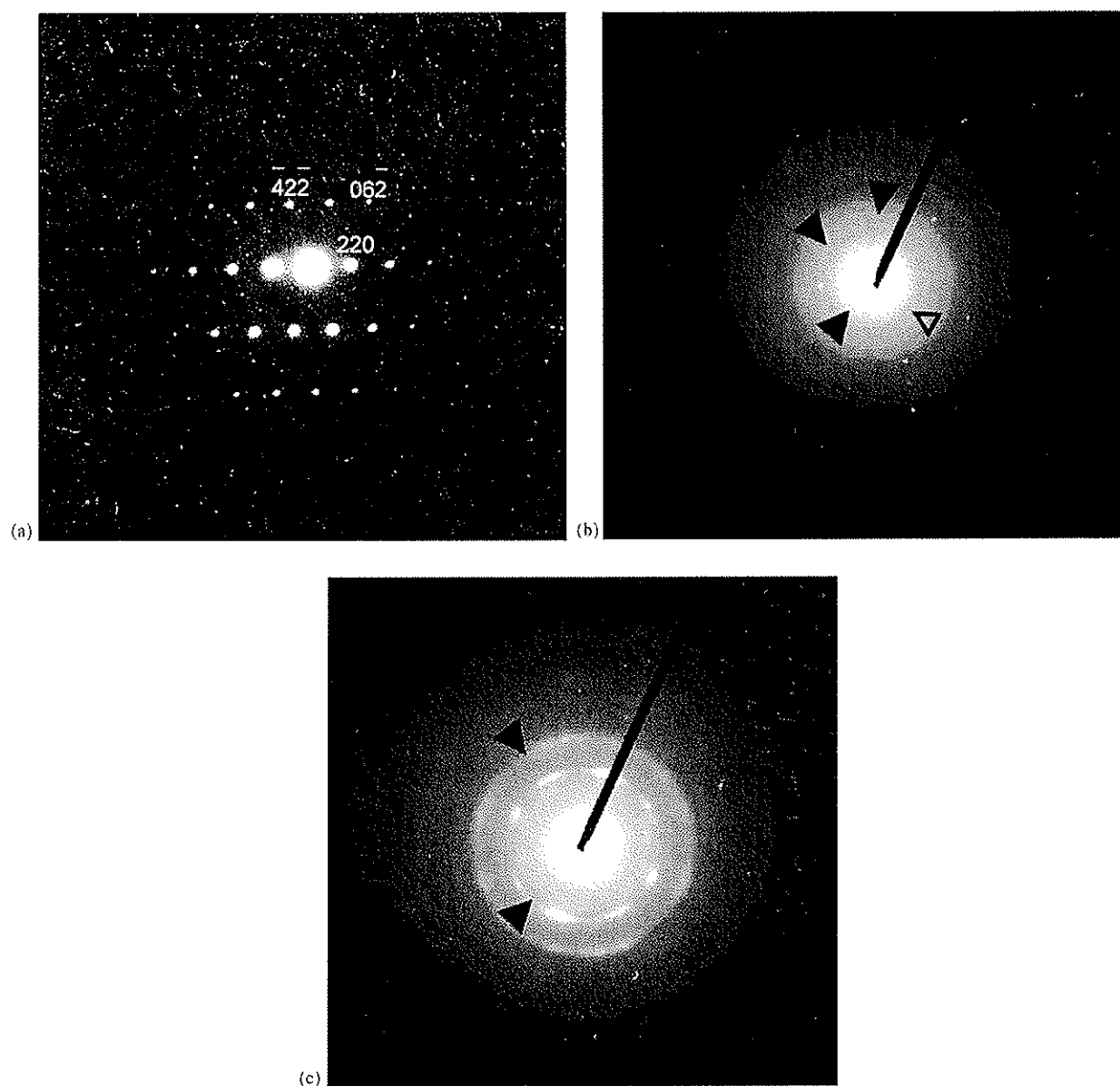
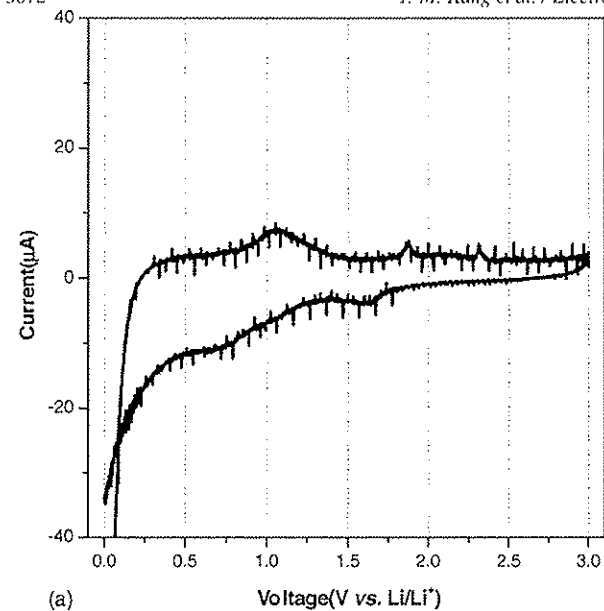


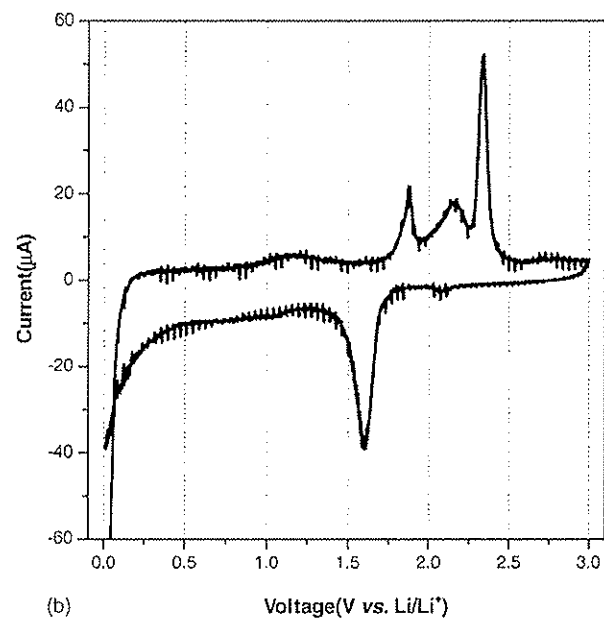
Fig. 4. SADP's (selected area diffraction patterns) for (a) as prepared Co_3O_4 , (b) Co_3O_4 in the charged state at the 100th cycle and (c) Co_3O_4 in the discharged state at the 100th cycle.

suit from the greatly reduced binding energy of Li_2O , which is due to the small particle size of Li_2O and the catalytic activity of transition metal (Co). Actually, it was generalized that the smaller particle size the material has, the lower melting point or binding energy it has [26]. Besides, because the transition metal, such as Co is currently used as the catalyst for not only the reduction of H_2 or O_2 on the surface of single wall nanotube [27] but also the decomposition of Li_2S [21], which 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), it can be envisaged that Co plays a crucial role in the formation or decomposition of Li_2O . However, up to now, it has never been made clear why Li_2O can be reversibly formed and de-

composed during charging and discharging of Co_3O_4 . So, to observe what kind of effect Co has on the reversible decomposition or formation of Li_2O , CV (cyclic voltammogram) graphs were obtained for Li_2O and a mixture of Li_2O -Co (90 wt.%:10 wt.%). As shown in Fig. 5(a), the CV plot of Li_2O has several oxidation peaks and reduction peaks. When Co was added to Li_2O , Fig. 5(b) shows that the oxidation and reduction peaks in the CV of the mixture of Li_2O -Co have much stronger intensity than those in the CV of Li_2O . Though, because it had not been elucidated what reaction is involved with the oxidation or reduction peaks in the CV of Li_2O , XRD analyses were performed at 1.75, 2, 2.25 and 2.5 V during the oxidation reaction (Li ion extraction) as well



(a)



(b)

Fig. 5. Cyclic voltammograms of (a) Li_2O and (b) Co added Li_2O . Addition of Co enlarges the intensities of the oxidation peak and the reduction peak.

as at 2.5, 1.8 and 1.25 V during the reduction reaction (Li ion insertion). From the XRD pattern in Fig. 6, it can be observed that while Li ions are being extracted, the Li_2O peak continues to decrease. On the other hand, while 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. From the difference between the CV of Li_2O and that of Li_2O -Co mixture in intensity, it can be inferred that Co has a significant catalytic activity that tends to activate the formation and decomposition of Li_2O . Therefore, it can be concluded that when Co_3O_4 is charged

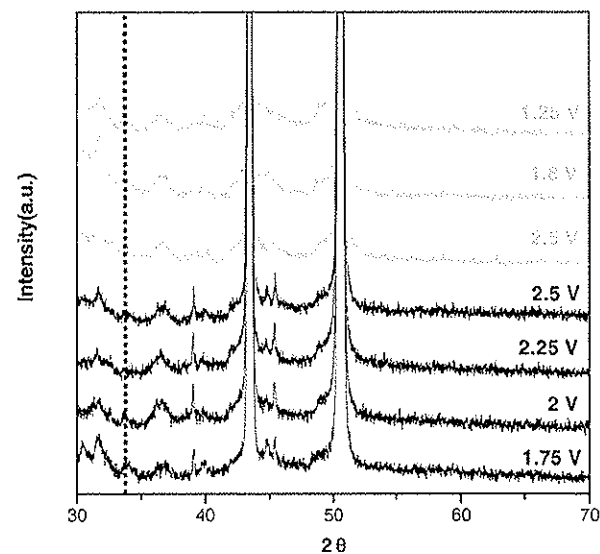


Fig. 6. XRD patterns for Li_2O 's at 1.75, 2, 2.25 and 2.5 V during the oxidation reaction (Li ion extraction, these figures have black color), and at 2.5, 1.8 and 1.25 V during the reduction reaction (Li ion insertion, these figures have gray color).

and discharged, the catalytic activity of Co enables an irreversible material, Li_2O , to form and decompose reversibly.

4. Conclusions

Transition metal oxides were initially only regarded as cathode materials, and their use as the anode material was ignored. However, since J.M. Tarascon et al. showed that transition metal oxides, such as Co_3O_4 , CoO , etc., are also very promising as anode materials, there has been more and more attention paid to them. Among all of these materials, Co_3O_4 shows the high capacity, around 700 mAh/g, twice as high as the commercial anode material, graphite. Moreover, except for the 1st cycle, Co_3O_4 retains good coulombic efficiency at every cycle, which leads to a good cycle life (93.4% of initial capacity is maintained after 100 cycles.). In general, Co_3O_4 has been reported to charge or discharge by the formation or decomposition of Li_2O . However, now that Li_2O is known to be an electrochemically irreversible material, we could wonder whether Co_3O_4 really charges or discharges by the formation or decomposition of Li_2O and if the formation or decomposition of Li_2O is the real mechanism behind the behavior of Co_3O_4 , what is the main reason why Li_2O forms or decomposes reversibly. EIS analyses showed that after the 1st cycle, the insertion or extraction of Li ion in Co_3O_4 can occur homogeneously and reversibly (randless-like behavior). When connecting these EIS analyses with SADP patterns after Li insertion or Li extraction at the 100th cycle, the results showed that the main homogeneous phase during Li ion insertion is a mixture of Co- Li_2O , while Co_3O_4 is the main phase during Li ion extraction. It

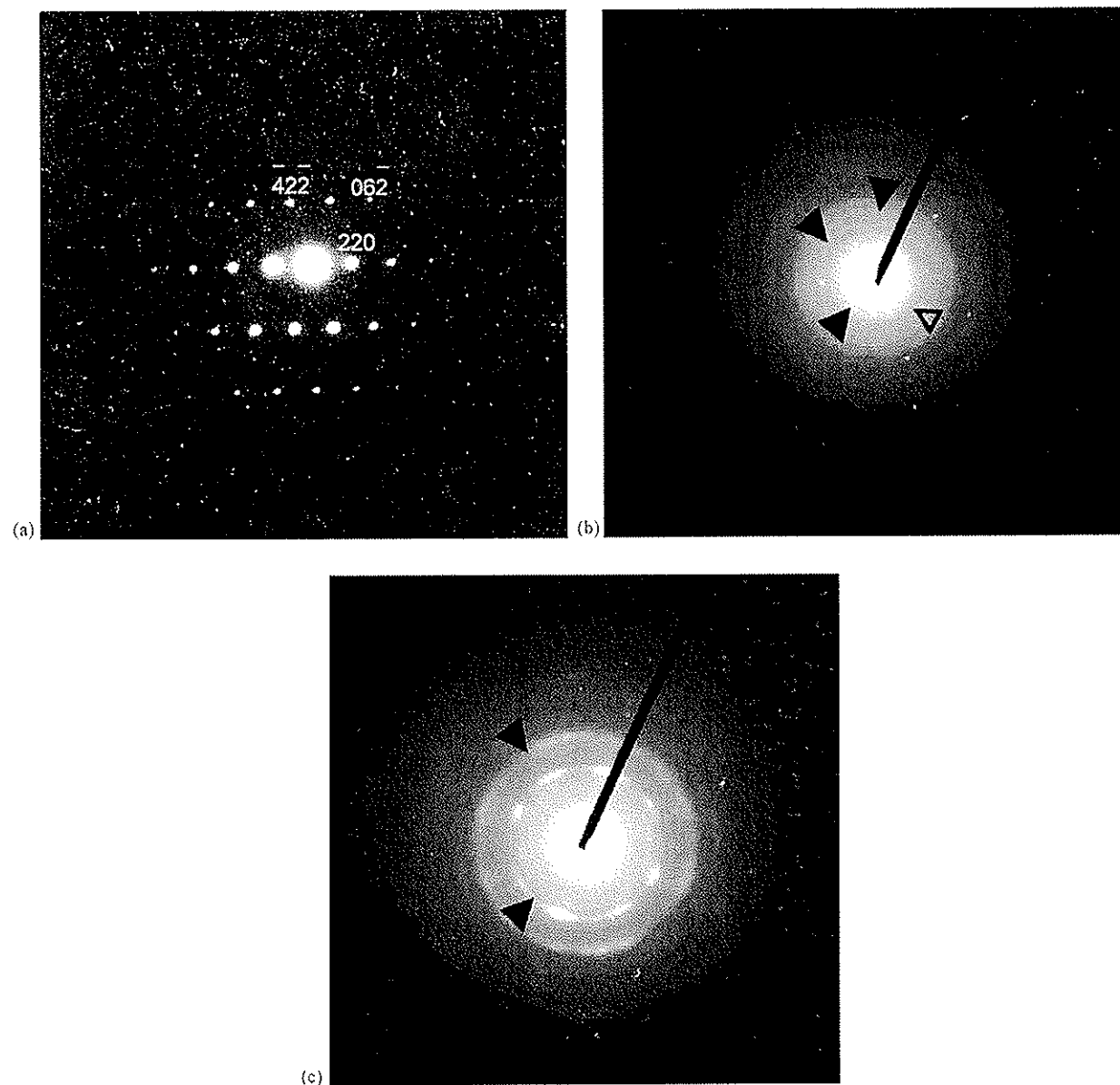
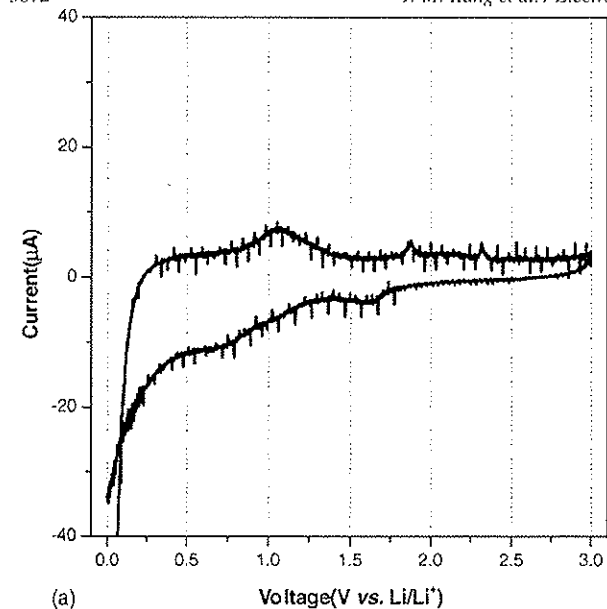


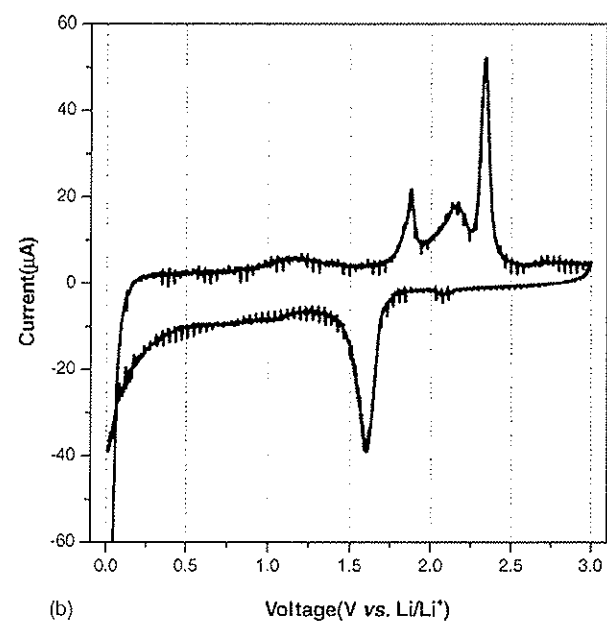
Fig. 4. SADP's (selected area diffraction patterns) for (a) as prepared Co_3O_4 , (b) Co_3O_4 in the charged state at the 100th cycle and (c) Co_3O_4 in the discharged state at the 100th cycle.

sult from the greatly reduced binding energy of Li_2O , which is due to the small particle size of Li_2O and the catalytic activity of transition metal (Co). Actually, it was generalized that the smaller particle size the material has, the lower melting point or binding energy it has [26]. Besides, because the transition metal, such as Co is currently used as the catalyst for not only the reduction of H_2 or O_2 on the surface of single wall nanotube [27] but also the decomposition of Li_2S [21], which 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), it can be envisaged that Co plays a crucial role in the formation or decomposition of Li_2O . However, up to now, it has never been made clear why Li_2O can be reversibly formed and de-

composed during charging and discharging of Co_3O_4 . So, to observe what kind of effect Co has on the reversible decomposition or formation of Li_2O , CV (cyclic voltammogram) graphs were obtained for Li_2O and a mixture of Li_2O -Co (90 wt.%:10 wt.%). As shown in Fig. 5(a), the CV plot of Li_2O has several oxidation peaks and reduction peaks. When Co was added to Li_2O , Fig. 5(b) shows that the oxidation and reduction peaks in the CV of the mixture of Li_2O -Co have much stronger intensity than those in the CV of Li_2O . Though, because it had not been elucidated what reaction is involved with the oxidation or reduction peaks in the CV of Li_2O , XRD analyses were performed at 1.75, 2, 2.25 and 2.5 V during the oxidation reaction (Li ion extraction) as well



(a)



(b)

Fig. 5. Cyclic voltammograms of (a) Li_2O and (b) Co added Li_2O . Addition of Co enlarges the intensities of the oxidation peak and the reduction peak.

as at 2.5, 1.8 and 1.25 V during the reduction reaction (Li ion insertion). From the XRD pattern in Fig. 6, it can be observed that while Li ions are being extracted, the Li_2O peak continues to decrease. On the other hand, while 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. From the difference between the CV of Li_2O and that of Li_2O -Co mixture in intensity, it can be inferred that Co has a significant catalytic activity that tends to activate the formation and decomposition of Li_2O . Therefore, it can be concluded that when Co_3O_4 is charged

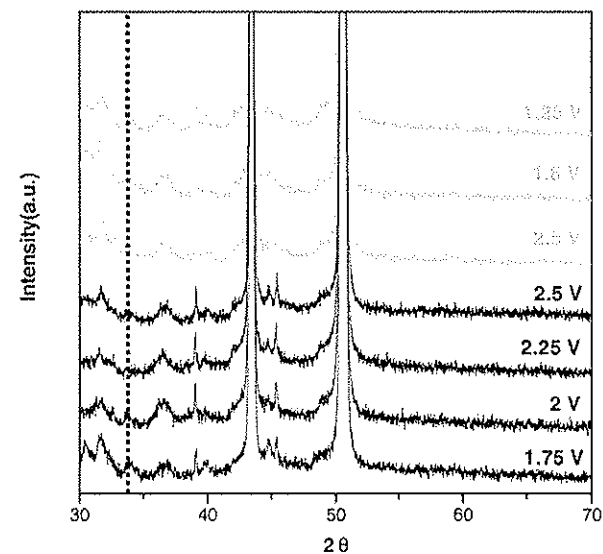


Fig. 6. XRD patterns for Li_2O 's at 1.75, 2, 2.25 and 2.5 V during the oxidation reaction (Li ion extraction, these figures have black color), and at 2.5, 1.8 and 1.25 V during the reduction reaction (Li ion insertion, these figures have gray color).

and discharged, the catalytic activity of Co enables an irreversible material, Li_2O , to form and decompose reversibly.

4. Conclusions

Transition metal oxides were initially only regarded as cathode materials, and their use as the anode material was ignored. However, since J.M. Tarascon et al. showed that transition metal oxides, such as Co_3O_4 , CoO, etc., are also very promising as anode materials, there has been more and more attention paid to them. Among all of these materials, Co_3O_4 shows the high capacity, around 700 mAh/g, twice as high as the commercial anode material, graphite. Moreover, except for the 1st cycle, Co_3O_4 retains good coulombic efficiency at every cycle, which leads to a good cycle life (93.4% of initial capacity is maintained after 100 cycles.). In general, Co_3O_4 has been reported to charge or discharge by the formation or decomposition of Li_2O . However, now that Li_2O is known to be an electrochemically irreversible material, we could wonder whether Co_3O_4 really charges or discharges by the formation or decomposition of Li_2O and if the formation or decomposition of Li_2O is the real mechanism behind the behavior of Co_3O_4 , what is the main reason why Li_2O forms or decomposes reversibly. EIS analyses showed that after the 1st cycle, the insertion or extraction of Li ion in Co_3O_4 can occur homogeneously and reversibly (randless-like behavior). When connecting these EIS analyses with SADP patterns after Li insertion or Li extraction at the 100th cycle, the results showed that the main homogeneous phase during Li ion insertion is a mixture of Co- Li_2O , while Co_3O_4 is the main phase during Li ion extraction. It

was thus confirmed that the formation and decomposition of Li_2O is the charge–discharge mechanism of Co_3O_4 . On the other hand, the CV of Li_2O –Co mixture shows much larger oxidation and reduction peaks than that of Li_2O . Based on XRD analyses, oxidation and reduction in the CV of Li_2O correspond to decomposition and formation of Li_2O , respectively. Hence, Co addition to Li_2O facilitates decomposition and formation of Li_2O . Finally, these results imply that during charging or discharging of Co_3O_4 , the catalytic effect of Co must be one of the main causes that make Li_2O form or decompose reversibly.

Acknowledgements

The authors wish to express thanks to the LG Chemical Ltd., Research Park, IREX, ARC (Australian Research Council) 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. Sawai, Y. Iwakoshi, T. Ohzuku, *Solid State Ionics* 69 (1994) 273.
- [2] J.R. Dahn, A.K. Sleight, H. Shi, J.N. Reimers, O. Zhong, B.M. Way, *Electrochim. Acta* 38 (1993) 1179.
- [3] R. Yazami, D. Guerard, *J. Power Sources* 43–44 (1993) 39.
- [4] Y. Idota, T. Kubota, A. Matsufuji, Y. Maekawa, T. Miyasaka, *Science* 276 (1997) 1395.
- [5] N. Tamura, R. Ohshita, M. Fujimoto, M. Kamino, S. Fujitani, *J. Electrochem. Soc.* 150 (2003) A679.
- [6] H.S. Kim, J.H. Choi, H.J. Sohn, T. Kang, *J. Electrochem. Soc.* 146 (1999) 4401.
- [7] N. Goldenfield, *J. Power Sources* 26 (1989) 121.
- [8] S.C. Levy, P. Bro, *Battery Hazards and Accident Prevention*, Plenum, New York, 1994.
- [9] D. Guyomard, C. Sigala, A. Le Gal La Salle, Y. Piffard, *J. Power Sources* 68 (1997) 692.
- [10] Y. Piffard, F. Leroux, D. Guyomard, J.L. Mansot, M. Tournoux, *J. Power Sources* 68 (1997) 698.
- [11] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.M. Tarascon, *Nature* 407 (2000) 496.
- [12] M. Winter, J.O. Besenhard, *Electrochim. Acta* 45 (1999) 31.
- [13] J.A. Courtney, J.R. Dahn, *J. Electrochem. Soc.* 144 (1997) 2045.
- [14] J. Yang, M. Winter, J.O. Besenhard, *Solid State Ionics* 90 (1996) 281.
- [15] N. Dimov, S. Kugino, M. Yoshio, *Electrochim. Acta* 48 (2003) 1579.
- [16] J. Niu, J.Y. Lee, *Electrochem. Solid-State Lett.* 5 (2002) A107.
- [17] 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.
- [18] J.R. Dahn, U.V. Sacken, C.A. Michal, *Solid State Ionics* 44 (1990) 87.
- [19] T. Ohzuku, M. Kitagawa, T. Hirai, *J. Electrochem. Soc.* 137 (1990) 769.
- [20] A. Yamada, M. Hosoya, S.C. Chung, Y. Kudo, K. Hinokuma, K.Y. Liu, Y. Nishi, *J. Power Sources* 119–121 (2003) 232.
- [21] P. Poizot, S. Laruelle, S. Grugeon, J.M. Tarascon, *J. Electrochem. Soc.* 149 (2002) A1212.
- [22] K. Wan, S.F.Y. Li, Z. Gao, K.S. Siow, *J. Power Sources* 75 (1998) 9.
- [23] D. Larcher, G. Sudant, J.B. Leriche, Y. Chabre, J.M. Tarascon, *J. Electrochem. Soc.* 149 (2002) A234.
- [24] Y.-M. Kang, K.-T. Kim, J.-H. Kim, H.-S. Kim, P.S. Lee, J.-Y. Lee, H.K. Liu, S.X. Dou, *J. Power Sources* 133 (2004) 252.
- [25] J.R. Macdonald, *Impedance Spectroscopy*, Wiley, 1987.
- [26] Buffat, D. Bonel, *J. Phys. Rev. A* 13 (1976) 2287.
- [27] R.I. Masel, *Principles of Adsorption and Reaction on Solid Surfaces*, John Wiley & Sons Inc., 1996.

was thus confirmed that the formation and decomposition of Li_2O is the charge–discharge mechanism of Co_3O_4 . On the other hand, the CV of Li_2O –Co mixture shows much larger oxidation and reduction peaks than that of Li_2O . Based on XRD analyses, oxidation and reduction in the CV of Li_2O correspond to decomposition and formation of Li_2O , respectively. Hence, Co addition to Li_2O facilitates decomposition and formation of Li_2O . Finally, these results imply that during charging or discharging of Co_3O_4 , the catalytic effect of Co must be one of the main causes that make Li_2O form or decompose reversibly.

Acknowledgements

The authors wish to express thanks to the LG Chemical Ltd., Research Park, IREX, ARC (Australian Research Council) 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. Sawai, Y. Iwakoshi, T. Ohzuku, *Solid State Ionics* 69 (1994) 273.
- [2] J.R. Dahn, A.K. Steigh, H. Shi, J.N. Reimers, O. Zhong, B.M. Way, *Electrochim. Acta* 38 (1993) 1179.
- [3] R. Yazami, D. Guerdar, *J. Power Sources* 43–44 (1993) 39.
- [4] Y. Idota, T. Kubota, A. Matsufuji, Y. Maekawa, T. Miyasaka, *Science* 276 (1997) 1395.
- [5] N. Tamura, R. Ohshita, M. Fujimoto, M. Kamino, S. Fujitani, *J. Electrochem. Soc.* 150 (2003) A679.
- [6] H.S. Kim, J.H. Choi, H.J. Sohn, T. Kang, *J. Electrochem. Soc.* 146 (1999) 4401.
- [7] N. Goldenfield, *J. Power Sources* 26 (1989) 121.
- [8] S.C. Levy, P. Bro, *Battery Hazards and Accident Prevention*, Plenum, New York, 1994.
- [9] D. Guyomard, C. Sigala, A. Le Gal La Salle, Y. Piffard, *J. Power Sources* 68 (1997) 692.
- [10] Y. Piffard, F. Leroux, D. Guyomard, J.L. Mansot, M. Tournoux, *J. Power Sources* 68 (1997) 698.
- [11] P. Poizot, S. Laruelle, S. Grugeon, L. Dupont, J.M. Tarascon, *Nature* 407 (2000) 496.
- [12] M. Winter, J.O. Besenhard, *Electrochim. Acta* 45 (1999) 31.
- [13] I.A. Courtney, J.R. Dahn, *J. Electrochem. Soc.* 144 (1997) 2045.
- [14] J. Yang, M. Winter, J.O. Besenhard, *Solid State Ionics* 90 (1996) 281.
- [15] N. Dimov, S. Kugino, M. Yoshio, *Electrochim. Acta* 48 (2003) 1579.
- [16] J. Niu, J.Y. Lee, *Electrochem. Solid-State Lett.* 5 (2002) A107.
- [17] 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.
- [18] J.R. Dahn, U.V. Sacken, C.A. Michal, *Solid State Ionics* 44 (1990) 87.
- [19] T. Ohzuku, M. Kitagawa, T. Hirai, *J. Electrochem. Soc.* 137 (1990) 769.
- [20] A. Yamada, M. Hosoya, S.C. Chung, Y. Kudo, K. Hinokuma, K.Y. Liu, Y. Nishi, *J. Power Sources* 119–121 (2003) 232.
- [21] P. Poizot, S. Laruelle, S. Grugeon, J.M. Tarascon, *J. Electrochem. Soc.* 149 (2002) A1212.
- [22] K. Wan, S.F.Y. Li, Z. Gao, K.S. Siow, *J. Power Sources* 75 (1998) 9.
- [23] D. Larcher, G. Sudant, J.B. Leriche, Y. Chabre, J.M. Tarascon, *J. Electrochem. Soc.* 149 (2002) A234.
- [24] Y.-M. Kang, K.-T. Kim, J.-H. Kim, H.-S. Kim, P.S. Lee, J.-Y. Lee, H.K. Liu, S.X. Dou, *J. Power Sources* 133 (2004) 252.
- [25] J.R. Macdonald, *Impedance Spectroscopy*, Wiley, 1987.
- [26] Buffat, D. Bonel, *J. Phys. Rev. A* 13 (1976) 2287.
- [27] R.I. Masel, *Principles of Adsorption and Reaction on Solid Surfaces*, John Wiley & Sons Inc., 1996.

