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

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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

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A study on the charge–discharge mechanism of Co$_3$O$_4$ as an anode for the Li ion secondary battery

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Abstract

Co$_3$O$_4$ 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$_3$O$_4$ can occur homogeneously and reversibly (random-like behavior; homogeneous mixture: Co–Li$_2$O (in the state of Li insertion), Co$_3$O$_4$ (in the state of Li extraction)). In fact, the coulombic efficiency of Co$_3$O$_4$ was almost 100% except for the 1st cycle. According to P. P. Poizat's research on several kinds of transition metal oxides, such as Co$_3$O$_4$, CoO, NO, etc., a small Li$_2$O particle size and catalytic activity of the transition metal are expected to decrease the binding energy of Li$_2$O tremendously. As a result, Li$_2$O should be easy to decompose, and transition metal oxides should be able to charge or discharge reversibly by formation or decomposition of Li$_2$O. However, this assumption has never been confirmed by experimental results. In our results, the CV (cyclic voltammetry) of a Li$_2$O–Co$_3$O$_4$ mixture shows much larger oxidation and reduction peaks than that of Li$_2$O. Based on XRD analysis, oxidation and reduction in the CV of Li$_2$O correspond, respectively, to the decomposition and formation of Li$_2$O. So, it can be asserted that Co addition to Li$_2$O facilitates decomposition and formation processes in Li$_2$O and that the catalytic effect of the transition metal must be one of the main causes that make Li$_2$O form or decompose repeatedly.

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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 tested at 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
volume expansion should be added [4,14]. In the first attempt, Sn alloys (SnCu, SnF3, 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/g), but 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 also be 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 CoO, Co3O4, 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] Pirlot et al. [11,21] summed that the reversible formation and decomposition of Li2O on transition metal oxides, such as CoO and Co3O4 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 CoO and Co3O4 can be charged or discharged by formation or decomposition of Li2O. Finally, several experimental works will be given to show 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 250 °C for 2 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-pyrrolidone (NMP) to make the slurry with appropriate viscosity. Carnauba wax was then used to coat the mixture. After the electrode was dried at 100 °C for 2 h in vacuum (10-3 Torr), it was compressed under a pressure of about 100 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 CoO4 electrode plays a role of the negative electrode (anode), Li ion insertion and extraction in CoO4 are related to the discharge and charge process, respectively. However, note that the charge and discharge process of CoO4 electrodes is named according to the full cell test where the CoO4 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 dimethyl carbonate (DEC).

The anode performance of the CoO4 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 Toscan 3000plus battery tester (Toyo system Corporation). In order to analyze the electrochemical impedence response, a Solution 1255 frequency response analyzer (FRA) was used in conjunction with the Solution 1266 electrochemical interface. After the electrode reached an equilibrium potential, the electrochemical impedence 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 (90 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
well as the change of Li2O 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 DMC to remove the residual LiPF6 and finally dried at 80°C. When the dried electrodes were subjected to TEM (transmission electron microscopy), the phase transition of Co3O4 during cycling was confirmed.

3. Results and discussion

3.1. General properties of Co3O4 as an anode material and the reason why the charge–discharge mechanism of transition metal oxides, such as Co3O4, should be clarified

In the current study, Co-oxide was manufactured from the solid-state reaction of Co(II) in air. The XRD pattern of Co oxide (Fig. 1) prepared from this reaction shows that this product corresponds to Co3O4. When Co3O4 is charged and discharged between 0.01 and 3.0 V, as shown in Fig. 2(a), Co3O4 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, Co3O4 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 whether Co3O4 can be charged and discharged by reversible formation and decomposition of Li2O, it should be verified why the formation and decomposition of Li2O are reversible during the charge and discharge of Co3O4. The reason of large initial irreversible capacity observed in Fig. 2(b) can be confirmed in our previous paper [24].
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 CoO or the mixture of Li$_2$O and Co at the previous cycles, cannot obstruct Li ion transfer anymore 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 random-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$_2$O$_4$ 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$_2$O$_4$ shows the obvious crystalline pattern having [113] as the zone axis, whereas in the Li inserted state at the 100th cycle, SADP is made up of several polycrystalline patterns (∥) 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$_2$O 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 (▽), which were found by the subsequent indexing to correspond to Co$_2$O$_4$. Therefore, it can be assumed that the homogeneous phases during Li insertion are a mixture of Li$_2$O 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$_2$O$_4$ can be expressed by this reaction connected to the formation or decomposition of Li$_2$O.

Li insertion process:

$$\text{Co}_2\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- \rightarrow 3\text{Co} + 4\text{Li}_2\text{O}$$

Li extraction process:

$$3\text{Co} + 4\text{Li}_2\text{O} \rightarrow \text{Co}_2\text{O}_4 + 8\text{Li}^+ + 8\text{e}^-$$

3.3. The main reason why Li$_2$O can be reversibly formed and decomposed during charging and discharging of Co$_2$O$_4$

In the previous section, it was shown that although Li$_2$O is a representative electrochemically irreversible material, Co$_2$O$_4$ is able to charge and discharge by the formation and decomposition of Li$_2$O. As for the reason why the reversible formation and decomposition of Li$_2$O are possible during charging and discharging of Co$_2$O$_4$, Pelotot et al. suggested that the reversible formation and decomposition of Li$_2$O re-

5.2. Reversible charge–discharge mechanism of Co$_2$O$_4$

For elucidating the reason why Li$_2$O can be reversibly formed or decomposed, above all, EIS analyses were conducted for Co$_2$O$_4$ 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$_2$O$_4$ 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.
well as the change of Li$_2$O 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$_3$O$_4$ during cycling was confirmed.

3. Results and discussion

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In the current study, Co$_3$O$_4$ was manufactured from the solid-state reaction of CoCO$_3$ in air. The XRD pattern of Co$_3$O$_4$ (Fig. 1) prepared from this reaction shows that this product corresponds to Co$_3$O$_4$. When Co$_3$O$_4$ is charged and discharged between 0.01 and 3.0 V, as shown in Fig. 2(a), Co$_3$O$_4$ 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$_3$O$_4$ 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 whether Co$_3$O$_4$ can be charged and discharged by reversible formation and decomposition of Li$_2$O, it should be verified why the formation and decomposition of Li$_2$O are reversible during the charge and discharge of Co$_3$O$_4$. The reason of large initial irreversible capacity observed in Fig. 2(b) can be confirmed in our previous paper [24].
3.2. Reversible charge–discharge mechanism of Co₃O₄

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 Co₃O₄ or the mixture of Li₂O 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 'null-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 Co₃O₄ is also able to charge or discharge in homogeneous phases. When SADPs (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 Co₃O₄ shows the obvious crystalline pattern having [113] as the zone axis, whereas in the Li inserted state at the 100th cycle, SADP is made up of several polycrystalline patterns (γ) and hollow rings (γ'). As a result of indexing, it was revealed that the polycrystalline patterns correspond to Co nanoparticles and the hollow rings occur due to Li₂O 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 (γ'), which were found by the subsequent indexing to correspond to CoO₃. Therefore, it can be assumed that the homogenous phases during Li insertion are a mixture of Li₂O amorphous phases and Co nanoparticles, and during Li extraction, Co oxides can be expected as the possible homogeneous phases. Based on these results, the reversible reaction of Co₃O₄ can be expressed by this reaction connected to the formation or decomposition of Li₂O.

Li insertion process:

\[ \text{Co₃O₄} + 8\text{Li}^+ + 8\text{e}^- \rightarrow 3\text{Co} + 4\text{Li}_2\text{O} \]

Li extraction process:

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3.3. The main reason why Li₂O can be reversibly formed and decomposed during charging and discharging of Co₃O₄

In the previous section, it was shown that although Li₂O is a representative electrochemically irreversible material, Co₃O₄ is able to charge and discharge by the formation and decomposition of Li₂O. As for the reason why the reversible formation and decomposition of Li₂O are possible during charging and discharging of Co₃O₄, P刈Tet et al. suggested that the reversible formation and decomposition of Li₂O re-
sult from the greatly reduced binding energy of Li$_2$O, which is due to the small particle size of Li$_2$O 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$_2$S [21], which has a similar bond enthalpy to Li$_2$O (bond enthalpy of Li$_2$S: 312.5 kJ/mol, bond enthalpy of Li$_2$O: 333.5 kJ/mol), it can be envisaged that Co plays a crucial role in the formation or decomposition of Li$_2$O. However, up to now, it has never been made clear why Li$_2$O can be reversibly formed and decomposed during charging and discharging of Co$_x$O$_{2-x}$. So, to observe what kind of effect Co has on the reversible decomposition or formation of Li$_2$O, CV (cyclic voltammogram) graphs were obtained for Li$_2$O and a mixture of Li$_2$O-Co (90 wt. %:10 wt. %). As shown in Fig. 5(a), the CV plot of Li$_2$O has several oxidation peaks and reduction peaks. When Co was added to Li$_2$O, Fig. 5(b) shows that the oxidation and reduction peaks in the CV of the mixture of Li$_2$O-Co have much stronger intensity than those in the CV of Li$_2$O. Though, because it had not been elucidated what reaction is involved with the oxidation or reduction peaks in the CV of Li$_2$O, XRD analyses were performed at 1.75, 2, 2.25 and 2.5 V during the oxidation reaction (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 pattern in Fig. 6, it can be observed that while Li ions are being extracted, the Li$_2$O peaks continue to decrease. On the other hand, while Li ions are being inserted, the Li$_2$O peak increases. From this result, it is easily confirmed that the oxidation peak and the reduction peak in the CV of Li$_2$O correspond to Li$_2$O decomposition and formation, respectively. From the difference between the CV of Li$_2$O and that of Li$_2$O-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$_2$O. Therefore, it can be concluded that when Co$_3$O$_4$ is charged and discharged, the catalytic activity of Co enables an irreversible material, Li$_2$O, 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$_3$O$_4$, 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$_3$O$_4$ shows the high capacity, around 700 mAh/g, twice as high as the commercial anode material, graphite. Moreover, except for the 1st cycle, Co$_3$O$_4$ 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$_3$O$_4$ has been reported to charge or discharge by the formation or decomposition of Li$_2$O. However, now that Li$_2$O is known to be an electrochemically irreversible material, we could wonder whether Co$_3$O$_4$ really charges or discharges by the formation or decomposition of Li$_2$O and if the formation or decomposition of Li$_2$O is the real mechanism behind the behavior of Co$_3$O$_4$, what is the main reason why Li$_2$O forms or decomposes reversibly. EIS analyses showed that after the 1st cycle, the insertion or extraction of Li ion in Co$_3$O$_4$ can occur homogeneously and reversibly (radius-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$_2$O, while Co$_3$O$_4$ is the main phase during Li ion extraction. It
Fig. 4. SADPs (selected area diffraction patterns) for (a) as-prepared CoOx, (b) CoOx in the charged state at the 100th cycle and (c) CoOx in the discharged state at the 100th cycle.

sult from the greatly reduced binding energy of Li$_2$O, which is due to the small particle size of Li$_2$O 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$_2$S [21], which has a similar bond enthalpy to Li$_2$O (bond enthalpy of Li$_2$S: 312.5 kJ/mol, bond enthalpy of Li$_2$O: 333.5 kJ/mol), it can be envisaged that Co plays a crucial role in the formation or decomposition of Li$_2$O. However, up to now, it has never been made clear why Li$_2$O can be reversibly formed and decomposed during charging and discharging of CoOx. So, to observe what kind of effect Co has on the reversible decomposition or formation of Li$_2$O, CV (cyclic voltammogram) graphs were obtained for Li$_2$O and a mixture of Li$_2$O-Co (50:50 wt%). As shown in Fig. 5(a), the CV plot of Li$_2$O has several oxidation peaks and reduction peaks. When Co was added to Li$_2$O, Fig. 5(b) shows that the oxidation and reduction peaks in the CV of the mixture of Li$_2$O-Co have much stronger intensity than those in the CV of Li$_2$O. Though, because it had not been elucidated what reaction is involved with the oxidation or reduction peaks in the CV of Li$_2$O, XRD analyses were performed at 1.75, 2, 2.25 and 2.5 V during the oxidation reaction (Li ion extraction) as well
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was thus confirmed that the formation and decomposition of Li$_2$O is the charge–discharge mechanism of Co$_3$O$_4$. On the other hand, the CV of Li$_2$O-Co mixture shows much larger oxidation and reduction peaks than that of Li$_2$O. Based on XRD analyses, oxidation and reduction in the CV of Li$_2$O correspond to decomposition and formation of Li$_2$O, respectively. Hence, Co addition to Li$_2$O facilitates decomposition and formation of Li$_2$O. Finally, these results imply that during charging or discharging of Co$_3$O$_4$, the catalytic effect of Co must be one of the main causes that make Li$_2$O form or decompose reversibly.

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was thus confirmed that the formation and decomposition of Li$_2$O is the charge-discharge mechanism of CoO$_2$. On the other hand, the CV of Li$_2$O-Co mixture shows much larger oxidation and reduction peaks than that of Li$_2$O. Based on XRD analyses, oxidation and reduction in the CV of Li$_2$O correspond to decomposition and formation of Li$_2$O, respectively. Hence, Co addition to Li$_2$O facilitates decomposition and formation of Li$_2$O. Finally, these results imply that during charging or discharging of CoO$_2$, the catalytic effect of Co must be one of the main causes that make Li$_2$O form or decompose reversibly.

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