

Investigation of cobalt oxides as anode materials for Li-ion batteries

G.X. Wang^{*}, Y. Chen, K. Konstantinov, Matthew Lindsay, H.K. Liu, S.X. Dou

*Energy Storage Materials Research Program, Institute for Superconducting & Electronic Materials,
University of Wollongong, Wollongong, NSW 2522, Australia*

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Abstract

Cobalt oxides are investigated as anode materials for lithium-ion (Li-ion) batteries by means of a variety of electrochemical characterization techniques. The CoO electrode demonstrates a stable reversible lithium storage capacity of about 300 mAh g⁻¹, even after 30 cycles. The reactivity of the cobalt oxides is attributed to the fact that the products of lithiation are in the form of nanosized products. © 2002 Published by Elsevier Science B.V.

Keywords: Li-ion battery; Cobalt oxide; Nanosize particles

1. Introduction

Lithium-ion (Li-ion) batteries have been emerging as power sources for modern electronics because they have the highest specific energy among all the rechargeable batteries, and have no memory effect. Present commercial lithium-ion batteries use LiCoO₂ or LiMn₂O₄ as cathode materials, and graphite or carbonaceous materials as anode materials [1]. Graphite anode materials have a theoretical gravimetric capacity of 372 mAh g⁻¹, or a volumetric capacity of 820 mAh cm⁻³ [2–4].

In recent years, a world-wide effort has been made to find alternative anode materials to replace graphite in Li-ion batteries. Idota et al. [5] have reported a new type of high capacity anode material that consists of tin-based amorphous oxides. The lithium reaction mechanism relies on the formation of Li–Sn alloys. Since then, tin-based oxides have been intensively investigated [6–8]. A large irreversible capacity prevents tin-based oxide anode materials from any practical application because the lithium source comes from the cathode material, e.g. LiCoO₂, which is limited in Li-ion cells. Therefore, the irreversible capacity of the anode must be made as small as possible.

Poizot et al. [9] recently proposed a class of new anode materials, namely, nano-sized transition-metal oxides such as nickel oxides, cobalt oxides and iron oxides for Li-ion batteries [9]. The mechanism of the lithium reaction differs from lithium insertion/extraction in graphite anodes or

lithium-alloying processes in tin-based oxides. The authors proposed a new mechanism which involves the formation and decomposition of Li₂O, with the reduction and oxidation of metal nano-particles.

In the present paper, a series of cobalt oxides as anode materials have been prepared, and their electrochemical properties have been systematically tested.

2. Experimental

CoO was synthesised by decomposition of CoCO₃ in an argon atmosphere at 850 °C for 12 h. Co₃O₄ was obtained by decomposition of CoCO₃ in air at 900 °C for 12 h. This type of Co₃O₄ is called HT-Co₃O₄. Fine Co₃O₄ powders were also prepared by heating Co(OH)₂ at low temperature (250 °C) under and oxygen flow for 20 h, this variety is referred to as LT-Co₃O₄. Superfine Co₃O₄ powders were prepared by high-energy ball milling. The ball milling was performed with a planetary ball-milling machine (Pulverisette-5, LABTECHNICS, Australia) for 120 h at a rotation rate of 200 rpm.

The physical properties of the prepared cobalt oxides were characterized by X-ray diffraction (XRD, MO3xHF22, MacScience Co. Ltd., Japan) and particle-size analysis (Mastersizer, Malvern Instruments Ltd.). The morphology of the cobalt oxide powders was examined with a scanning electron microscope (SEM, Leica/Cambridge Steroscan 440 scanning electron microscope).

Teflon test cells were fabricated to evaluate the electrochemical properties of cobalt oxide anodes in Li-ion cells.

^{*} Corresponding author. Fax: +61-2-4221-5731.
E-mail address: gwang@uow.edu.au (G.X. Wang).

The cobalt oxide electrodes were made by dispersing 85 wt.% active material, 13 wt.% carbon black and 2 wt.% polyvinylidene fluoride (PVDF) binder in dimethyl phthalate solvent to form a slurry, which was then spread on to a copper foil. The thickness of the electrode was approximately 50–60 μm with a loading of 1–2 mg. The cells were assembled in an argon filled glove-box (Mbraun, Unilab, USA). The electrolyte was 1 M LiPF_6 in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume, provided by MERCK KgaA, Germany). The cells were galvanostatically charged and discharged at a current density of 20 mA g^{-1} , and showed voltage behaviour over the voltage range 0.01–3.0 V versus Li/Li^+ . Cyclic voltammetry (CV) was performed to determine the characteristics of the lithium reaction with the cobalt oxide electrodes. The CV measurements were performed by

means of a potentiostat (Model M362, EG&G Princeton Applied Research, USA) at a slow scanning rate of 1 mV s^{-1} .

3. Results and discussion

The three different types of Co_3O_4 powders were characterized by XRD and SEM observations. The XRD patterns are shown in Fig. 1(a). The HT- Co_3O_4 is a crystalline powder which has intense and sharp diffraction peaks. The corresponding electron micrograph (Fig. 2(a)) shows the oxide to have a circular crystals. During the high-temperature heating process, the Co_3O_4 crystals grow sufficiently in a certain direction, which indicates that a liquid phase exists at the crystal boundaries at high temperature. LT- Co_3O_4 has very

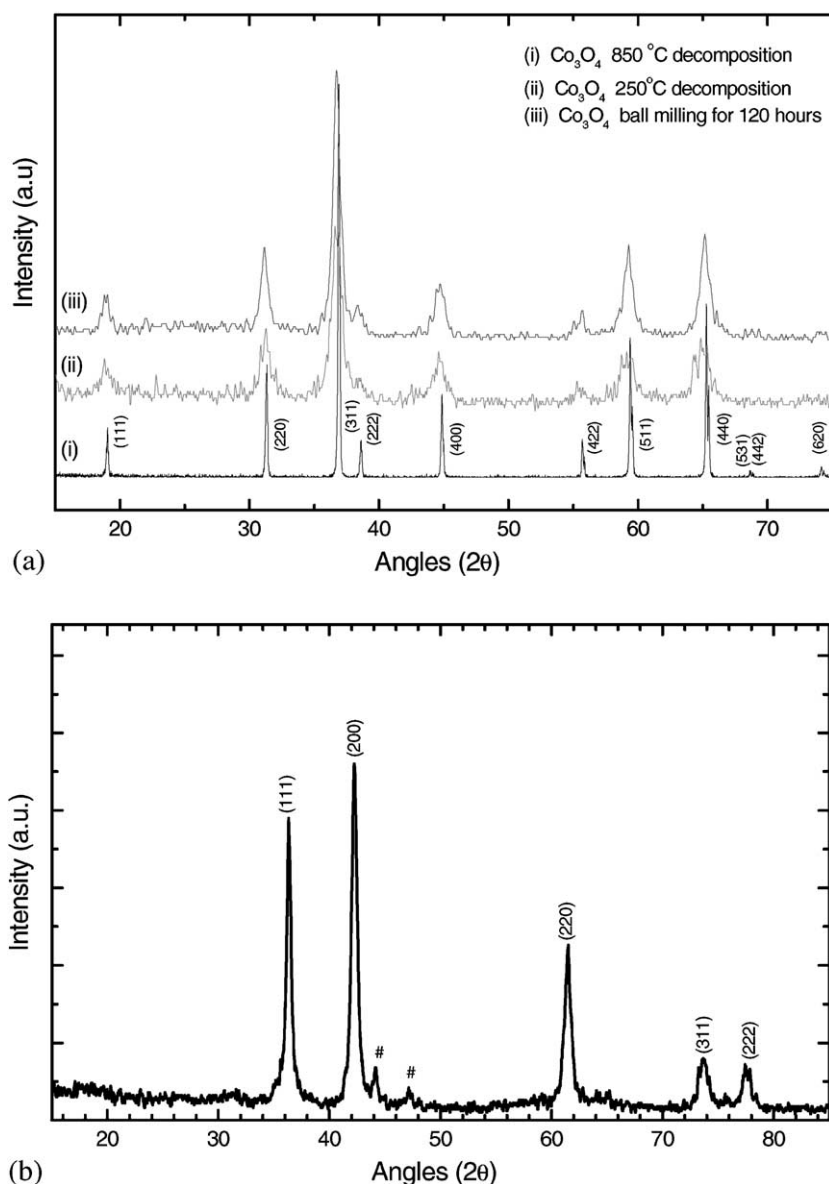


Fig. 1. X-ray diffraction patterns of cobalt oxides. (a) The varieties of Co_3O_4 ; (b) CoO plus impurity phase.

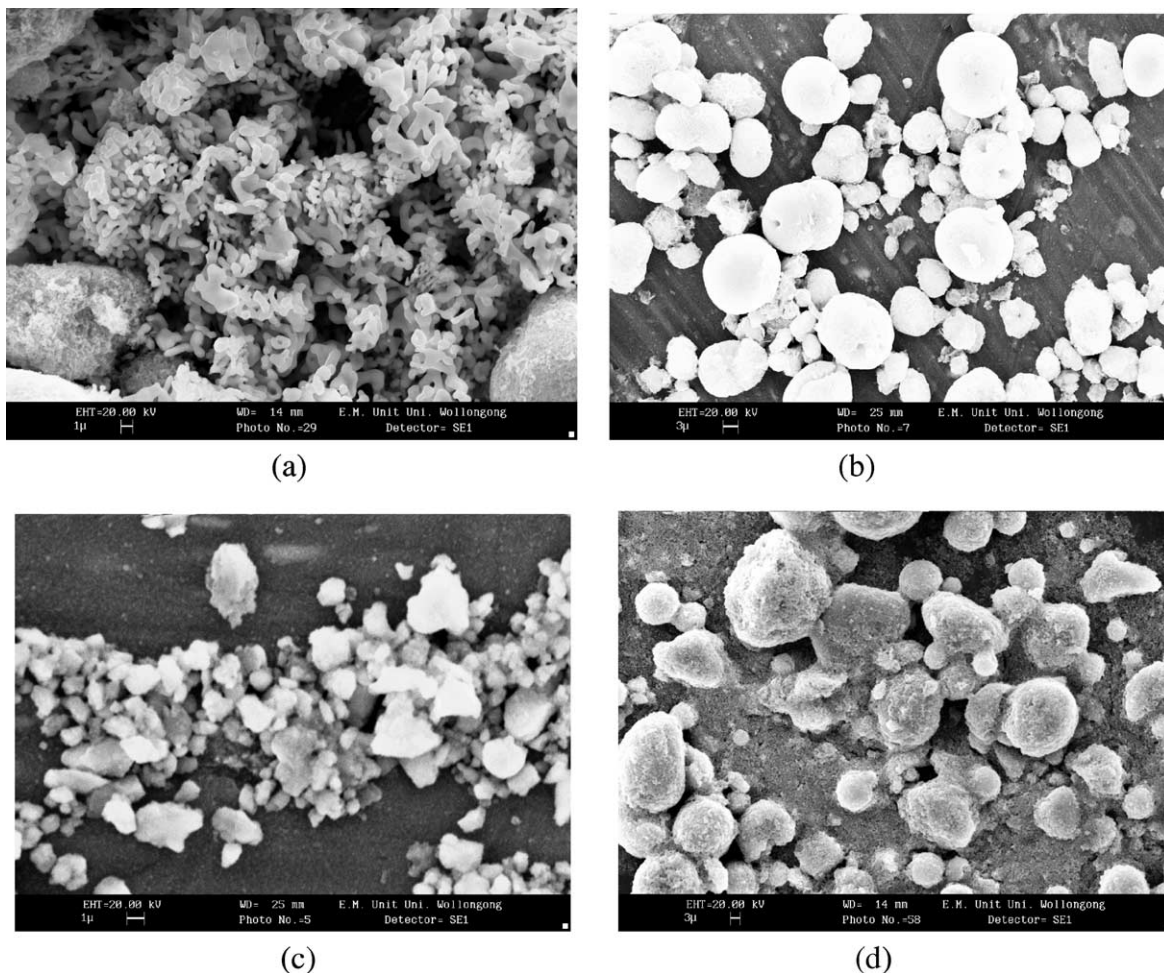


Fig. 2. SEM images of (a) HT- Co_3O_4 ; (b) LT- Co_3O_4 ; (c) ball-milled Co_3O_4 ; (d) CoO.

broad diffraction lines (Fig. 1(a)) which suggests poor crystallinity. An electron micrograph of LT- Co_3O_4 (Fig. 2(b)) reveals spheric agglomerates with included pores. When the precursor CoCO_3 is heated at low temperature, CoCO_3 is decomposed to cobalt oxide and carbon dioxide. Due to the 'blowing effect' of CO_2 gas, tiny pores are formed inside the Co_3O_4 particles. At 250°C , the Co_3O_4 crystals cannot grow sufficiently. Thus, the pores are permanently trapped inside the particles to form a porous material. After high-energy ball milling, the well crystalline HT- Co_3O_4 becomes a cotton-shaped agglomerate with poor crystallinity (as shown in Fig. 2(c)). This is typically demonstrated by the XRD pattern (Fig. 1(a)) which displays broad diffraction peaks. Cobalt monoxide was obtained by heating CoCO_3 at 900°C under argon flow. The corresponding X-ray diffraction pattern is shown in Fig. 1(b). A small amount of cubic Co_3O_4 (Fd3m), as an impurity phase, is found in the cobalt monoxide. The electron micrograph (Fig. 2(d)) demonstrates that CoO powders easily form agglomerates with very fine crystals. The crystal morphology is quite different from that of HT- Co_3O_4 (Fig. 2(a)).

The average particle size ($D(v, 0.5)$) of the cobalt oxides is 30, 16, 4.65 and 26 μm for HT- Co_3O_4 , LT- Co_3O_4 , ball-

milled Co_3O_4 and CoO, respectively. The measured particle size is the agglomerate size. The real crystalline size is much smaller, and is in the range of a few micrometers.

The discharge curves of the cobalt oxide electrodes in Li-ion test cells are given in Fig. 3. When discharging, the potentials of the cobalt oxide electrodes immediately falls to $< 1.25\text{ V}$, and then declines down to the cut-off voltage of 0.01 V . For Co_3O_4 electrodes, a discharge plateau exists between 1.0 and 0.75 V , whereas the discharge plateau for the CoO electrode is in the range $0.75\text{--}0.25\text{ V}$. These phenomena are further demonstrated in cyclic voltammograms for the electrodes (v.i.). For the ball-milled Co_3O_4 electrode, a large discharge plateau exists at $\sim 1.0\text{ V}$, as shown in Fig. 3(a), which is related to the formation of a solid electrolyte interface (SEI) on the surface of the electrode. Because ball-milled Co_3O_4 has a large surface area, it is likely that a passivation film is formed during the first discharge process. The discharge plateau is absent from the second cycle onwards. The lithium, which is consumed to form the SEI is not reversible. The retention of capacity with cycling the different oxide electrodes is shown in Fig. 4. The ball-milled Co_3O_4 electrode displays the highest irreversible capacity in the first cycle and the fastest rate of capacity

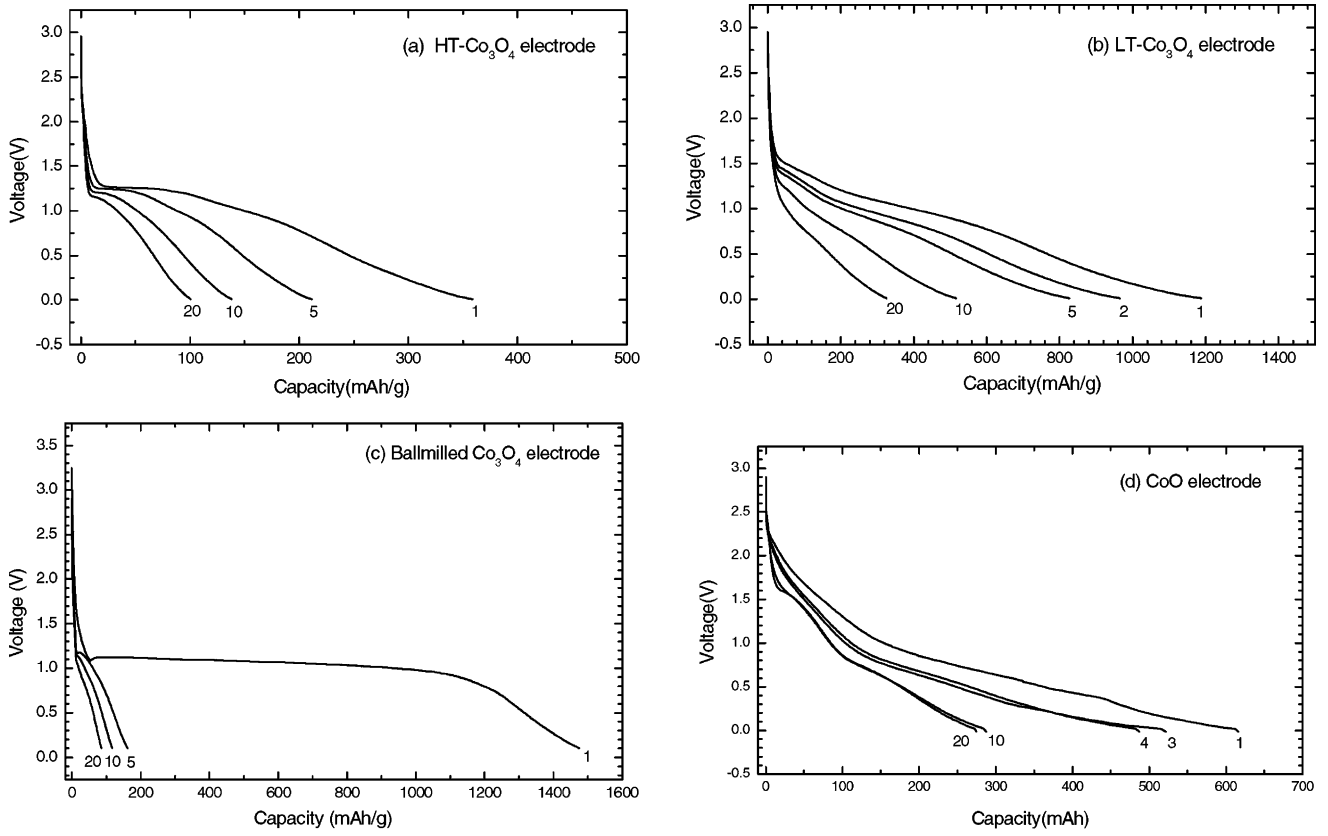


Fig. 3. Discharge profiles of cobalt oxide electrodes in Li-ion test cells, current density: 20 mA g⁻¹.

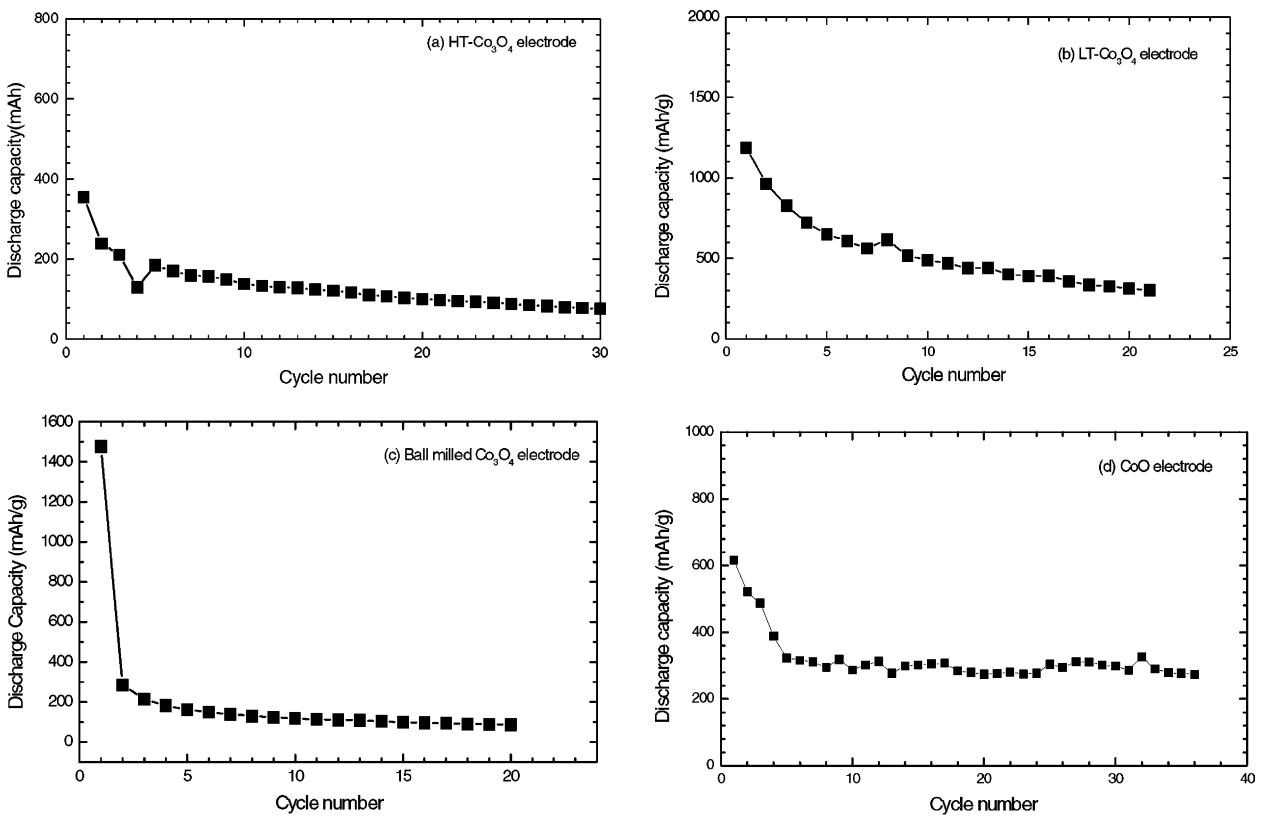


Fig. 4. Discharge capacity of cobalt oxide electrodes versus cycle number.

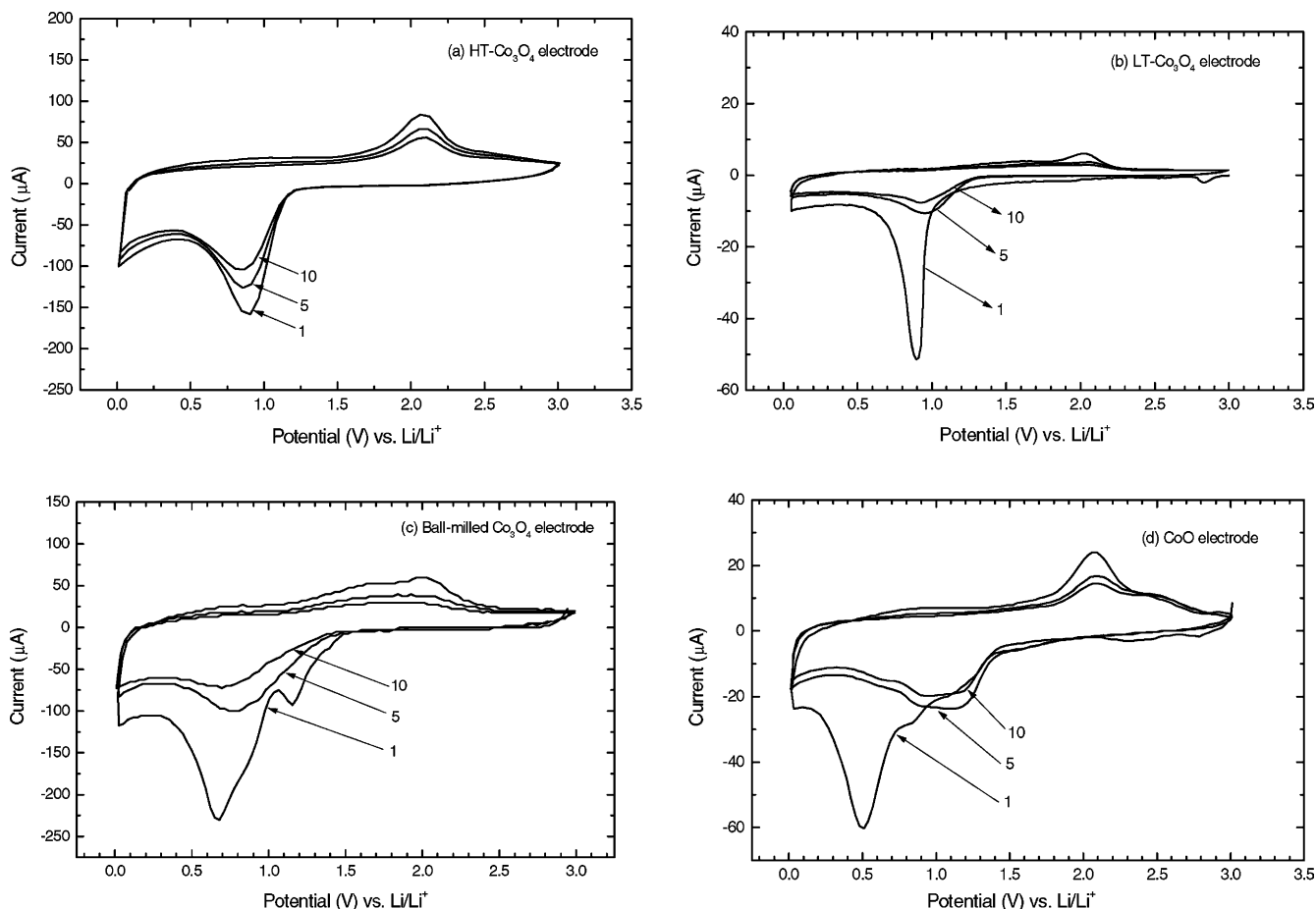


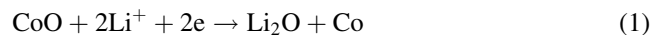
Fig. 5. Cyclic voltammograms of cobalt oxide electrodes in Li-ion cells. Scanning rate: 1 mV s^{-1} .

decay. The $\text{LT-Co}_3\text{O}_4$ and CoO electrodes have relatively good capacity retention. In particular, the CoO electrode retained about 300 mAh g^{-1} after the fifth cycle. This suggests that mono-cobalt oxide as is a promising material for the storage of lithium.

The CV curves for four different types of cobalt oxide electrodes are presented in Fig. 5. All cobalt oxide electrodes show one reduction and one oxidation peak in the potential range of $0.01\text{--}3.0 \text{ V}$ versus Li/Li^+ . This indicates that only one redox reaction is proceeding during the insertion and extraction of Li-ions. The reduction peaks for the HT- and $\text{LT-Co}_3\text{O}_4$ electrodes are at the same voltage in the voltammograms. By contrast, the reduction peaks of the ball-milled Co_3O_4 and CoO electrodes are shifted to a lower potential. This means that the mechanism of lithium reaction with HT- and $\text{LT-Co}_3\text{O}_4$ is different from that with ball-milled Co_3O_4 and Co electrodes. The oxidation peaks for all four types of cobalt oxide electrodes are unchanged. All cobalt oxide electrodes exhibited hysteresis between the lithiation and the de-lithiation processes, which is similar behaviour to that shown by tin oxide anode materials [10,11]. The four types of cobalt oxide electrodes exhibit different electrochemical behaviour in Li-ion cells. Therefore, the electrochemical performance of cobalt

oxides is dependent on their crystallinity, morphology and microstructure.

Poizot et al. [9] have proposed that the reaction mechanism of cobalt oxide with lithium in Li-ion cells is a displacive redox reaction, as follows.



Hence, by adding Eq. (1) and Eq. (2), we get the following Eq. (3):



The reaction of Li-ions with cobalt oxide to form lithium oxide and cobalt is thermodynamically feasible. Li_2O is, however, electrochemically inactive. Therefore, to extract lithium from Li_2O is thermodynamically impossible. Poizot et al. [9] argued that the chemical and physical phenomena are strongly affected when dealing with nano-sized materials. Electrochemically formed Li_2O and Co are in the form of nano-particles. With decreasing particle size, an increasing proportion of the total number of atoms lies near or on the surface, which makes the electrochemical reactivity of the nano-particles more and more important. In this

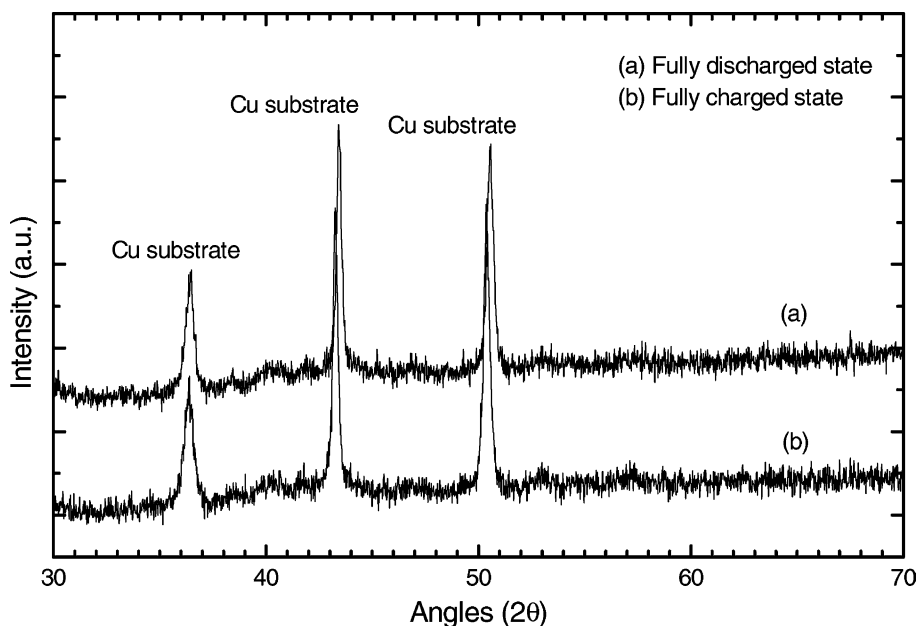


Fig. 6. Ex situ X-ray diffraction patterns of (a) HT- Co_3O_4 electrode in fully discharged state; (b) HT- Co_3O_4 electrode in fully charged state.

investigation, ex situ X-ray diffraction has been performed on the HT- Co_3O_4 electrode in the fully lithiated and the fully de-lithiated states, respectively. To obtain the fully lithiated state, a freshly assembled $\text{Co}_3\text{O}_4/\text{Li}$ cell was galvanostatically discharged to 0.01 V and then potentiostatically held at 0.01 V for 4 h. Similarly, the fully de-lithiated state was obtained by galvanostatically charging a $\text{Co}_3\text{O}_4/\text{Li}$ cell to 3.0 V and then potentiostatically holding at 3.0 V for 4 h. The test cells were disassembled in a glove-box. The Co_3O_4 electrodes were then taken out and the electrolyte on the surface of the electrode was removed and wiped out using dry cotton. The electrodes were then sealed with a polyethylene plastic film for X-ray diffraction. The ex situ XRD patterns are shown in Fig. 6, in which only the diffraction peaks from the copper substrate can be identified. In the fully lithiated state, the products would be Li_2O and Co, while in the fully de-lithiated state cobalt oxide should exist. In fact, Li_2O , Co and Co_3O_4 have not been detected. This demonstrates that the cobalt oxide loses crystallinity and the electrochemically formed lithiated products Li_2O and Co are in the form of nano-particles. Such particles possibly make it possible to extract lithium from Li_2O . Therefore, the cobalt oxide electrode displays a certain reversible lithium-storage capacity.

4. Conclusions

Four different types of cobalt oxide are investigated as lithium-storage materials in Li-ion cells. Electrochemical

testing demonstrates that cobalt oxide electrodes have the capability to react with lithium reversibly to a certain extent. LT- Co_3O_4 and CoO show good capacity retention on charge–discharge cycling, which is promising for their use as anode materials in Li-ion cells. Results from ex situ XRD studies on the Co_3O_4 electrode verified that Li_2O and Co, the products of lithiation, are nano-particles. The electrochemical properties of cobalt oxides are dependent on the crystallinity, morphology and particle size of the oxides. Optimization of the microstructure of cobalt oxides can improve their electrochemical performance.

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