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Short communication

Synthesis and reversible lithium storage of Cr_2O_5 as a new high energy density cathode material for rechargeable lithium batteries

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HIGHLIGHTS

- ► Pure Cr_2O_5 is prepared by the thermal decomposition of CrO_3 under ambient atmosphere at 350–400 °C.
- ► Reversible lithiation/de-lithiation of Cr_2O_5 proceeds via a single phase process.
- ► Cr_2O_5 electrode can reach a high energy density of 819 Wh kg^{-1} with good cyclability and high energy efficiency (83%).

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ABSTRACT

Chromium trioxide is calcined from 350 to 400 °C yielding pure Cr_2O_5. The electrochemical properties of the resulting chromium oxides have been measured in the potential range 2.0–4.5 V (vs. Li^+/Li) when used in lithium batteries. The first discharge process, the intercalation of lithium into Cr_2O_5, proceeds via two steps. In the following cycles, lithium is found to be reversibly de-lithiated/lithiated via a solid solution process with an un-known single phase $Li_xCr_2O_5$ (*u*-phase) characterized by an X-ray diffractive lattice spacing of about 0.20 nm. The sample that results from chromium trioxide being calcined at 350 °C shows the highest capacity of 273 mAh g^{-1} (the first discharge at 0.5 C rate) and the sample calcined at 400 °C shows the best cyclability with the capacity retention of 96% after 100 cycles. The energy density of Cr_2O_5 can reach 819 Wh kg^{-1} with the energy conversion efficiency of 83%.

1. Introduction

Transition metal oxides have attracted increasing interests as electrode materials of rechargeable lithium batteries for their high specific capacities of usually over 500 mAh g^{-1} compared with the theoretical 372 mAh g^{-1} of the state-of-the-art graphite. Most of these oxides, such as NiO [1–3], CoO [4–6] and CuO [7–9], can only be used as anodes due to their low working potentials (around 1.0 V vs. Li). However, high valence transition metal oxides, such as VO_x (VO_2 [10,11], V_2O_5 [12,13]) and MoO_3 [14], can react with lithium at a potential over 2.0 V vs. Li, and thus can be potentially used as cathode materials. Different from the situation of NiO or CoO, where lithiation process proceeds via a conversion reaction mechanism [15], lithium can reversibly intercalate into and de-intercalate from VO_x and MoO_3 during the charge and discharge processes. Their initial capacity loss is much lower and energy efficiency is much higher than those of CoO, NiO and CuO, due to the different lithium storage mechanism. Some high valence chromium oxides such as Cr_8O_{21}, Cr_3O_8 and CrO_2 can also store Li via intercalation reaction mechanism, and thus are promising cathode materials for their high specific capacities of over 200 mAh g^{-1} [16–21]. Another interesting high valence chromium oxide for reversible lithium intercalation is Cr_2O_5 [22–24], which is found as the main component of so-called “Seloxcette” or the product of CrO_3 intercalation in graphite [24]. However, the synthesis of the high valence chromium oxides usually carried out in an autoclave under high oxygen pressure, which is relatively difficult and dangerous. Also, without appropriately defining the potential range, the electrochemical cyclability of these chromium oxides is relatively poor. In this work, we calcine CrO_3 to synthesize Cr_2O_5 in only ambient conditions at the temperatures from 350 °C to 400 °C. It operates via a not reported solid solution process in the

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potential range 2.0–4.5 V (vs. Li^+/Li) and gives good performance with an energy density as high as 819 Wh kg^{-1}.

2. Experimental

Chromium oxides were synthesized via the thermal decompositions of a commercial CrO_3 powder (Sinopharm Chemical Reagent Co., Ltd) at various temperatures from 300 °C to 425 °C in air for 2 h. After the heat treatment, the products were ground in an agate mortar into fine powders. Thermogravimetric analysis (TGA) was applied to investigate the decomposition process of CrO_3 at the heating rate of 3 °C min^{-1} in air. The crystal structures of the decomposition products were characterized by X-ray diffraction (XRD, CuKα radiation, DX-2700).

The electrochemical performance of the obtained samples was measured in the CR2032 coin-type half cells with 1 M $LiPF_6$ in EC:DMC (1:1 v/v) as the electrolyte. The electrodes consisted of a mixture of 80 wt% chromium oxides, 10 wt% carbon black and 10 wt% PVDF binder on Al foil. The cells were assembled in an argon-filled dry-box (MBraun Labmaster 130) and cycled on a multi-channel battery test system (NEWARE BTS-610) at the constant current in the voltage range from 2.0 to 4.5 V. Cyclic voltammograms (CV) of the cells were also measured on a CHI 660 Electrochemical Workstation in the voltage range from 2.0 to 4.5 V at the scanning rate of 0.1 mV s^{-1}.

To investigate the lithium intercalation process into Cr_2O_5, an ex-situ XRD analysis was carried out on the sample obtained at 350 °C. The cells were cycled at C/16 (0.1 mA) and were disassembled at different charge–discharge states. The lithiated electrodes were washed by dimethyl carbonate (DMC) to remove the electrolyte residue. After drying in the argon-filled glove box, the XRD analyses of these electrodes were immediately performed in dry air with a scan rate of 1° min^{-1}.

3. Results and discussion

TGA curve (Fig. 1a) shows the thermal decomposition process of CrO_3. CrO_3 starts to decompose at around 250 °C and ends at 475 °C. The step-like TG curve indicates that the decomposition of CrO_3 can be roughly divided into two stages: (1) from 250 to 400 °C, the weight loss is 18%; (2) from 400 to 475 °C, the corresponding weight loss is 13%. According to the XRD patterns (Fig. 1b), Cr_8O_{21} and Cr_2O_5 are formed at 300 °C. Pure Cr_2O_5 is obtained in the temperature range from 350 to 400 °C but it further decomposes into Cr_2O_3 at 425 °C. Obviously, the weight loss in the first TG stage (18%) is markedly higher than the value (8%) predicted based on the conversion from CrO_3 to Cr_2O_5. This is due to the volatilization of CrO_3 at temperatures above its melting point 196 °C, as also observed by Liu et al. [18]. On the other hand, the weight loss in the second stage matches very well with the theoretical value because $M(Cr_2O_5)/M(Cr_2O_3) = 1.21 \approx 82\%/69\%$, meaning that the results of TGA and XRD agree with each other. As an example of the decomposition products from CrO_3, the morphology of Cr_2O_5 sample obtained at 375 °C (Fig. 1a) shows that the powder is composed of flaky particles.

Because the samples calcined at 350 °C to 400 °C are Cr_2O_5, which has not been investigated as a cathode material for lithium batteries, they are then focused in this work. Their first discharge and charge profiles (Fig. 2a) indicate that the first discharge process can be divided into two parts: (1) a short voltage slope from 3.2 to 2.9 V; (2) a long voltage plateau at about 2.9 V. The short slope should be related to a solid solution process and the plateau should be related to a two-phase reaction. It is noticed that the first discharge capacity decreases with increasing the calcination temperature. All of these Cr_2O_5 samples exhibit good cycling performance (Fig. 2b). Particularly, the 400 °C-calcined sample delivers a high capacity of 220 mAh g^{-1} with the best cycling performance.

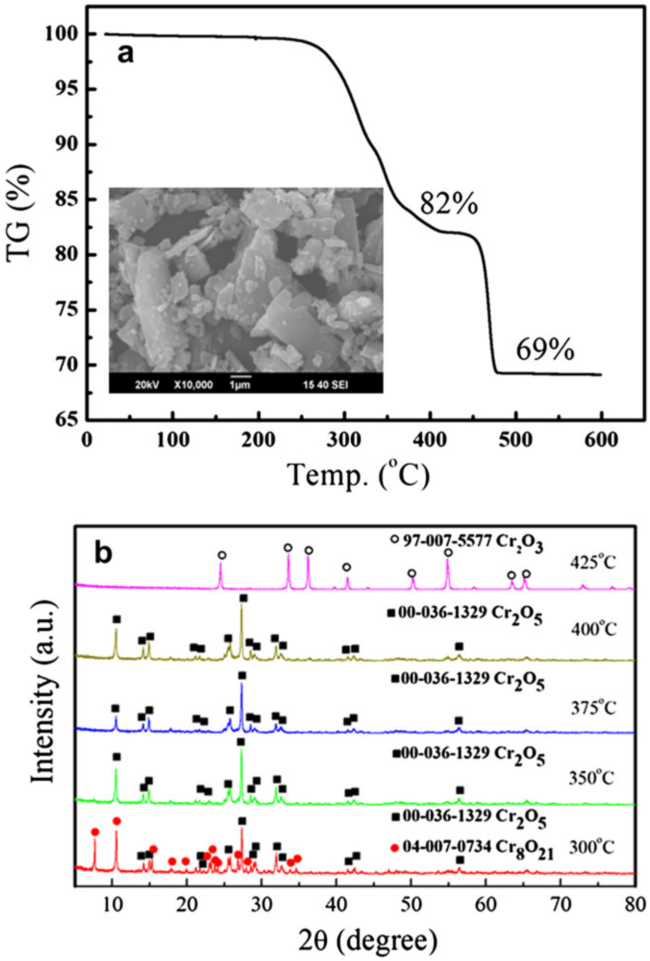

Fig. 1. TG curve (a) of CrO_3 and XRD patterns (b) of calcined samples.

To investigate the lithium intercalation process into Cr_2O_5, an ex-situ XRD analysis were carried out on the sample calcined at 350 °C (Fig. 3). From state A to B in the first discharge process, the peak at about 27° (marked with #) becomes weaker and the peaks at 28° and 30° grow wider and combine together. Nevertheless, there is a very minor change when discharged from A to B. From the state B to F, a new peak at around 45° (marked with *) is detected and its intensity increases with lithium intercalation, while other peaks become weaker and weaker until they disappear. This phenomenon implies that during the states from B to F, Cr_2O_5 reacts with lithium to form an un-identified phase (u-phase $Li_xCr_2O_5$) with a characteristic diffraction peak at around 45°. According to Bragg's law, this diffraction angle ($2\theta = 45°$) corresponds to a lattice spacing of about 0.20 nm. Based on the voltage profile (Fig. 3a), the lithiated sample at 2.0 V (state F) should be $Li_{2.2}Cr_2O_5$.

In the following charge process (from state F to K in Fig. 3), the diffraction peak at around 45° remains but shifts by 0.2° to the higher angle direction, suggesting that the de-lithiation is via a solid solution process of the u-$Li_xCr_2O_5$. The ex-situ XRD results are further confirmed by the CV curve (Fig. 2c). In the first cycle, there are two reduction peaks at 3.0 V and 2.8 V, and only one oxidation peak at 3.7 V. In the following cycles, the CV curves are almost overlapped, indicating that the lithiation/de-lithiation processes are highly reversible (Fig. 2d). After full charge, the