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Rotor blade grinding and re-annealing of $LiCoO_2$: SEM, XPS, EIS and electrochemical study

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Abstract

The layered particles of lithium cobalt oxide ($LiCoO_2$) have been modified using rotor blade grinding, re-annealing, and a combination of both treatments. SEM, XPS and EIS were used to study the effects of these treatments on the $LiCoO_2$ particles, and changes in electrochemical behaviour in the 4-V region vs. Li^+/Li were explored. After short grinding times (20 min), primary layered particles formed larger aggregates and poor electrochemical behaviour was observed. After 60 min grinding, $LiCoO_2$ showed a net improvement in reversible specific capacity and capacity retention, which is due to the formation of ultrafine layered particles. Further grinding up to 180 min lead to surface carbonation, increased impedances and poor electrochemical performance. Re-annealing improved the electrochemical behaviour of both ground and unground $LiCoO_2$. The best electrochemical behaviour was observed after grinding for 60 min and then re-annealing at 850 °C, which is linked with a low charge transfer resistance. XPS measurements revealed that the particles surface remained unchanged after heating to 500 °C, while heating to 850 °C eliminated surface carbonates, and prolonged grinding yielded extended surface carbonation.

Keywords: Battery; XPS; Ac impedance; Galvanostatic

1. Introduction

Lithium cobalt oxide ($LiCoO_2$) and related compounds are the most widely-used options as cathode materials for commercial lithium-ion batteries [1–4]. Cobalt substitution and particle surface treatments have been previously used to control the electrochemical properties of this layered-type oxide. The surface properties of $LiCoO_2$ particles have a direct influence on the electrochemical behaviour of the oxide [4,5]. Different preparation methods can be used to obtain fine particles of this ordered layered-type oxide [6–8]. On the other hand, grinding has been used to obtain or modify several active electrode materials through mechanical energy transfer [9], such as graphite [10], and $LiCoO_2$ and $LiNiO_2$ [11–13]. Thus, the rotor-blade grinding method can be used to modify hexagonal graphite and the resulting material displays an increased relative content of the rhombohedral polytype and improved electrochemical performance [10]. It has been demonstrated that $LiCoO_2$ can be transformed into a more disordered structure by ball milling for several hours, leading to enhanced cell polarization and capacity fade [12].

The aim of this study is to examine the effects of rotor-blade grinding and re-annealing of $LiCoO_2$. The influence of microtexture on electrochemical behaviour is discussed. XPS is used to study the particles' surface.

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Rotor blade milling for 60 min and re-annealing are shown here to induce positive transformations that improve electrochemical behaviour.

2. Experimental

A commercial $LiCoO_2$ sample (Aldrich, Lot #20804PR) was used as the starting material in this study. The X-ray diffraction data showed that this sample is a high purity material. The lithium cobalt oxide powder was dispersed in N-methyl pyrrolidone (NMP) and the resulting slurry was ground in an Ultra Turrax-T18 apparatus working at 10.000 r.p.m in air atmosphere. The high-speed rotating movement of the blades favours the exfoliation process. It should be noted that rotor blade grinding is "shear-mode", while ball-milling is mainly "impact-mode". NMP was removed by heating to 120 °C in air for several hours. Ground samples were obtained after milling for 20, 45, 60, 80, and 180 min periods. In addition, the starting $LiCoO_2$ material and selected ground samples were re-annealed at 500/850 °C in static air atmosphere for 48 h inside an alumina crucible. Heating and cooling rates were ca. $2° min^{-1}$. Scanning electron microscope (SEM) micrographs were obtained in a JSM63000 apparatus.

In order to obtain the electrodes for the electrochemical experiments, the $LiCoO_2$ active material (77%) was mixed with PVDF (8%) and graphite (15%), and dispersed in NMP. After heating to 150 °C in a vacuum for several hours, the resulting composite electrodes were supported on Al-foil and used as positive electrodes in lithium cells. The electrochemical behaviour of $LiCoO_2$-based positive electrodes was studied in lithium cells. In the Swagelok™-type cells, negative electrode consisted of a clean 9 mm diameter lithium metal disk. The commercial (Merck LP40) electrolyte solution was 1 M $LiPF_6$ in a 1:1 mixture of ethylene carbonate (EC) and diethyl carbonate (DEC), which was supported in Whatman™ glass microfibers as separators. Potentiostatic experiments were carried out with a MacPile-II instrument, by applying potential steps of 10 mV every 0.1 h in the range between 4.3 and 3.2 V.

Electrochemical impedance spectroscopy (EIS) experiments were carried out in three-electrode cells, using a PGSTAT12 Autolab instrument. The ac impedance spectra were recorded using a signal with an amplitude of 5 mV and frequency ranging from 100 kHz to 10 mHz. The working electrode was an 8 mm diameter disc containing about 2 mg of active material. The counter and reference electrodes were Li discs. The spectra were recorded at 3.9 V of the discharge process, after cell relaxation. The impedance spectra were represented after normalization to the $LiCoO_2$-weight; this means that the intrinsic resistances (in Ω units) have been multiplied by the active mass (in g units) of the electrode [14].

The XPS experiments were carried out at room temperature in a multichamber ultra high vacuum (UHV) system with the surface analysis system (Phi 5700). The base pressure during the measurements was over 10^{-9} mbar. AlKα radiation ($h\nu = 1486.6$ eV) from a monochromatized X-ray source was used for XPS.

3. Results and discussion

3.1. Electron microscopy

The changes in particle size and morphology induced by rotor-blade grinding of $LiCoO_2$ powders were followed by SEM. The as-received commercial $LiCoO_2$ sample exhibits particles with flat surfaces (Fig. 1); many of these particles are layered, and most of them have a thickness of between 2 and 20 μm. These particles are grouped in agglomerates of about 50 μm diameter. After 20 min of grinding, the most relevant feature is that some of the particles are partially fragmented, and primary layers with a thickness of about 100–400 nm are revealed inside. This is a preliminary stage of an extended exfoliation process, which is observed by increasing the grinding period to 45–80 min. Particle size reduction and platelike habit extend progressively, and some particles that are smaller than 1 μm are observed on the surface of larger particles. After 80 min grinding, most layered particles have a thickness of between 100 nm and 1 μm, while dimensions of over 10 μm are still observed in the basal plane surfaces. The most finely dispersed material will be henceforth referred to as ultrafine layers or nanolayered $LiCoO_2$. After 180 min grinding, the layered character is less evident and the particles have coalesced into secondary agglomerates with very irregular shapes and surface roughness. This is indicative of an extended carbonation process, as discussed below. The freshly cleaved surfaces that are created by grinding are reactive towards the atmosphere. The occurrence of lithium carbonate in ball-milled $LiCoO_2$ has been previously reported [12]. It should be remarked that a small amount of Li_2CO_3 has positive effects on battery safety [1,15]. However, an extended degradation of the surface can increase the impedance of the electrochemical cell [4,5].

The samples that were previously ground for 0, 60, 80 and 180 min were annealed at 500 and/or 850 °C for 2 days (Fig. 1). In the samples previously ground for 60–80 min, the particles retain a layered character after annealing at 850 °C, although the thicknesses of all the observed layers was apparently over 1 μm. The main differences between re-annealing at 500 and 850 °C are that particles smaller than 1 μm are not observed and the particles display flatter and smoother surfaces at the higher temperature. The particles of the sample previously ground for 180 min also recovered a layered-type character after re-annealing at 850 °C.