Influence of the $LiCoO_2$ particle size on the performance of lithium-ion batteries

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Abstract

Lithium cobalt oxide, $LiCoO_2$, of different particle-size distributions, has been studied in the $Li/LiCoO_2$ rechargeable battery system. The particle size influences the cycle stability. Upon cycling, the voltage drop contributed to the ohmic and polarization of charge/discharge processes were evaluated by current interrupt method.   © 1997 Published by Elsevier Science S.A.

1. Introduction

Lithium-ion batteries have become a potential product in rechargeable batteries [1,2]. So far, many efforts have been devoted to improving their cell performance. Lithium cobalt oxide, $LiCoO_2$, is one of the most promising cathode materials in Li-ion secondary batteries [3]. The performance of the batteries is affected by a number of factors, such as crystalline phase, elemental composition, particle size; the influence of the particle size on the cycle stability is not yet elucidated. In this work, cell performance and rate capabilities were studied with different $LiCoO_2$ particle size distributions by using charge and discharge recycling process; the particles have almost similar surface area. During cycling, their voltage changes were also measured by the current interruption method.

2. Experimental

Two $LiCoO_2$ electrodes with different particle size distributions (2–4 and 5–10 μm) were used as the cathodes in this study. The cathode electrodes were prepared by mixing $LiCoO_2$ material, acetylene black (AB) and polyvinyldiene fluoride (PVDF). The electrochemical behavior of $LiCoO_2$ was examined in a coin cell. The electrolyte solution was a mixture of ethylene carbonate (EC) and diethylene carbonate

(DEC) with 1 M $LiPF_6$. The water content of the electrolyte was less than 20 ppm. Cycling tests were performed by, first, galvanostatically charging at a certain C rate to a 4.1 V cutoff voltage followed by potentiostatically charging, and then galvanostatically discharged to a 2.8 V cutoff voltage at the same C rate. The current interrupt method was applied for 20 s at successive intervals during charge and discharge processes in order to elucidate the contributions of both IR and polarization voltage changes.

3. Results and discussion

The discharge capacity curves of $Li/LiCoO_2$ cells prepared from two $LiCoO_2$ compounds with different partcle sizes are shown in Fig. 1. The cycle stability of $LiCoO_2$ (2–4 μm) was better than that of $LiCoO_2$ (5–10 μm) for all C rates. Other properties such as lattice parameters obtained from least-square refinement and specific surface area were basically the same:

2–4 μm	$a = 2.815$ Å	$c = 14.051$ Å	0.78 m²/g
5–10 μm	$a = 2.812$ Å	$c = 14.027$ Å	0.79 m²/g

In addition, their scanning electron microscopy (SEM) graphs revealed similar morphology and the inductively coupled plasma (ICP) results showed the same composition of $Li_{0.94}CoO_2$. The observed poorer cycling behavior of 5–10 μm $LiCoO_2$ was therefore attributed to its larger particle size distribution. Diffusion of Li ion inside the $LiCoO_2$ particle
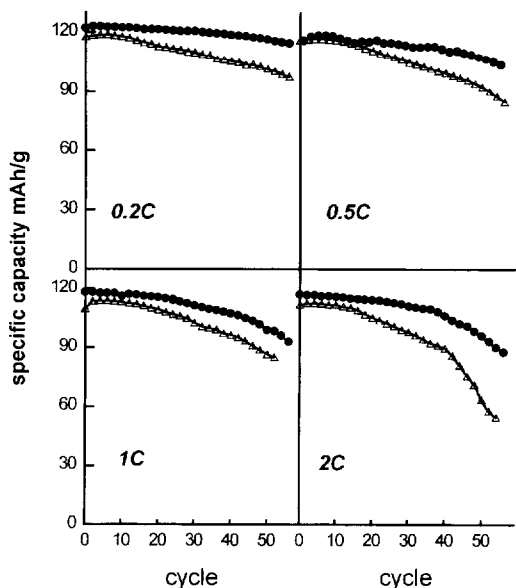
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Fig. 1. LiCoO₂ particle size effect on cycle stabilities: (○) 2–4 μm, and (△) 5–10 μm.

probably played a role in the cycling differentiation, further investigation was conducted by impedance measurements. Concerning their rate capabilities, their specific capacities (mAh/g) at different C rates were compared by averaging capacities from cycle no. 2 to cycle no. 6 and are listed in Table 1. The averaged specific capacity of $0.5C$, $1C$ and $2C$ was referred to which of $0.2C$ rate by percentage and were shown inside the parentheses. It is observed that both the 2–4 μm and the 5–10 μm LiCoO₂ gave comparable rate capabilities in our study. SEM studies on the 2–4 μm and the 5–10 μm LiCoO₂ revealed that both the 2–4 μm and the 5–10 μm LiCoO₂ were constructed by smaller fine LiCoO₂ particles sizing around 1 μm and this might account for the similar estimated rate capability but still different cycle stability.

It was often found that the voltage increasement/decreasement in charge/discharge curves became larger upon cycling, no matter which LiCoO₂ particle size was tested. This might indicate an increase in cell impedance and therefore more current interrupt experiments were conducted. Fig. 2 shows the charge and discharge curves of Li/LiCoO₂, 2–4 μm and 5–10 μm, with current interruptions at selected Δx intervals. The symbol Δx represents the Li composition change of LiCoO₂ when compared to its charged or dis-

charged state at that cycle. A series of straight lines in Fig. 2 indicates the voltage change at each current interrupt. Individual studies confirmed that it was affected by both IR and polarization parts within the chosen time interval. The voltage changes increased after 50 cycles revealing IR and polarization to be an important cause of Li/LiCoO₂ capacity degradation upon cycling. This phenomenon also depends on the C rates. The voltage change of the first current interrupt (those indicated by arrows) on the discharge curves of four C rates are plotted in Fig. 3. Empty and full symbols represent the voltage changes of 2–4 μm or 5–10 μm Li/LiCoO₂ cell at cycles nos. 2 and 50, respectively. Generally, the voltage changes increased monotonically with the C rates and non-
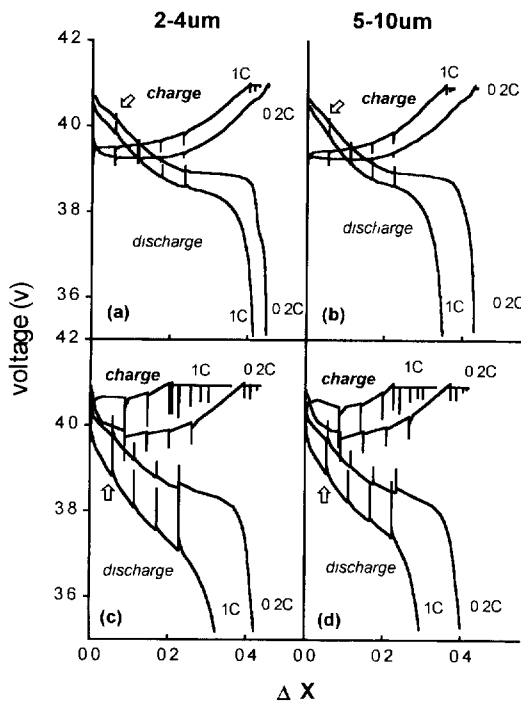

Fig. 2. Charge/discharge curves of LiCoO₂ with current interrupt (a), (c) 2–4 μm cycle no 2 and (b) cycle no 50; (c), (d) 5–10 μm cycle no. 2 and cycle no. 50.
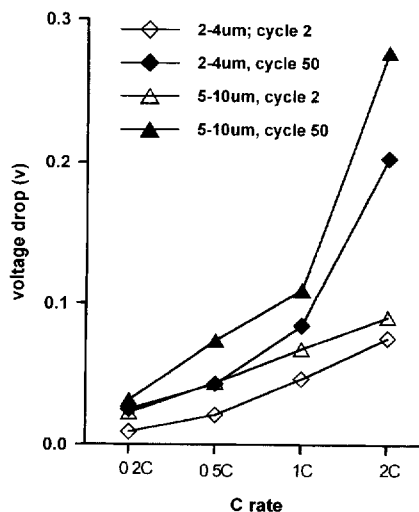
Table 1

Averaged specific capacities [a] at different cycling rates of 2–4 μm and 5–10 μm LiCoO₂ particle size distribution

	C rate			
	0.2C	0.5C	1C	2C
2–4 μm	122.1 (100%)	119.2 (98%)	118.4 (97%)	117.1 (96%)
5–10 μm	119.1 (100%)	117.0 (98%)	115.1 (97%)	114.0 (96%)

[a] The average of discharge specific capacity from cycle no 2 to cycle no. 6 (5 cycles)

Fig 3 Voltage change measured by the current interrupt method

linearly with the cycles. For all C rates, 5–10 μm $LiCoO_2$ displayed higher voltage variation than 2–4 μm $LiCoO_2$ throughout cycling, which probably contributed to its poorer cycle stability discussed previously.

4. Conclusions

The rate capability and cycle stability of $LiCoO_2$ with different particle size distributions have been evaluated and the results show that smaller particle size distribution has a better cycle stability but no difference on the rate capability has been observed. Further investigation by the current interrupt method disclosed that the increase in cell IR and polarization upon cycling is an obvious cause of cycle degradation.

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