

Cycle-life improvement of Li/LiCoO₂ batteries

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Abstract

The inherently good electronic conductivity and high lithium mobility of Li_xCoO₂ make it a prime candidate cathode material for high-power rechargeable lithium batteries. We have studied the ageing of Li/LiCoO₂ cells with LiPF₆ in propylene carbonate electrolyte during cycling between fixed voltage limits. The polarization increases with cycle number and the useful capacity decreases by 0.5 to 1% per cycle. Although some of the results seem to reflect a structural change of Li_xCoO₂, analysis of the data shows that degradation of the electrolyte is a more likely explanation for both the increase in polarization and the apparent structural change. Reduction of the maximum voltage from 4.3 to 4.1 V results in a lower initial capacity, but also in a higher remaining capacity after 100 cycles.

Keywords: Rechargeable lithium batteries; Cobalt oxide; Cycle life

1. Introduction

The long-term criteria of the US Advanced Battery Consortium (USABC) for electric-vehicle batteries of 200 Wh/kg (at a C/3 discharge rate) and 400 W/kg (at 80% depth-of-discharge for 30 s) can hardly be met but by lithium batteries. Candidate cathode materials for room temperature operation are the lithium-3d-metal oxides LiMO₂, where M stands for Mn, Ni, Co or a combination of these elements. Among these candidates LiCoO₂ offers advantages like ease of preparation, structural stability and high lithium-diffusion velocity. Its main disadvantage is the high price of cobalt.

The theoretical capacity of LiCoO₂ equals 274 Ah/kg, but severe degradation has been reported when more than 50% of the lithium content of LiCoO₂ was withdrawn [1,2]. Oxidation of the electrolyte and structural instability of Li_xCoO₂ for $x < 0.5$ are mentioned as explanations for the increase in polarization which reduces the effective capacity with cycling. The aim of this work is to elucidate the degradation mechanism and to find remedies which may increase the cycle life of batteries with Li_xCoO₂ cathodes.

2. Experimental

Test cells have been made in a Teflon housing with lithium foil anode, LiCoO₂ cathode and a 1 M solution

of LiPF₆ in propylene carbonate (PC) electrolyte. The separator is a glass microfibre filter. Stainless steel is used for the current collectors. A cathode tape is made from LiCoO₂ powder ($D_{50} = 13 \mu\text{m}$) with 1.2 wt.% binder (poly(ethylene oxide)). Circular samples of 10 mm diameter are cut from the tape and pressed to obtain cathodes with 30% porosity and 50 μm thickness.

Test cells are cycled between fixed voltage limits with constant current at a temperature of 25 °C. At the end of charge or discharge the cell is left to rest for at least 5 min. At more or less regular time intervals cycling is interrupted for inspection of data and a.c. impedance measurements. Relaxation of the cell voltage after charge or a short current pulse has been monitored. All cycling experiments have been performed in duplicate.

3. Results and discussion

The capacity of test cells versus number of cycles is shown in Fig. 1 for voltage limits of 4.1 or 4.3 V on charge and 3.3 V on discharge. Initially, a 1 mA current on charge corresponds approximately to a C/2 rate. At this rate the capacity left after 100 cycles is equal for cells charged to 4.1 and 4.3 V, even though the latter has 35% more initial capacity. At a lower rate, the capacity loss is less severe but still larger for the higher operating voltage.

Fig. 2 shows the relaxation of the cell voltage after 4 min/1 mA current pulses for a fresh cell and the

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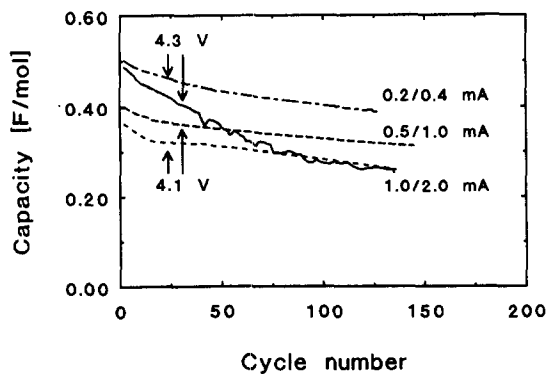


Fig. 1. Capacity of $\text{Li}/\text{Li}_x\text{CoO}_2$ cells cycled between 3.3 and 4.1 V or 4.3 V with charge and discharge currents, as indicated. Cathode and anode areas are about 0.8 cm^2 .

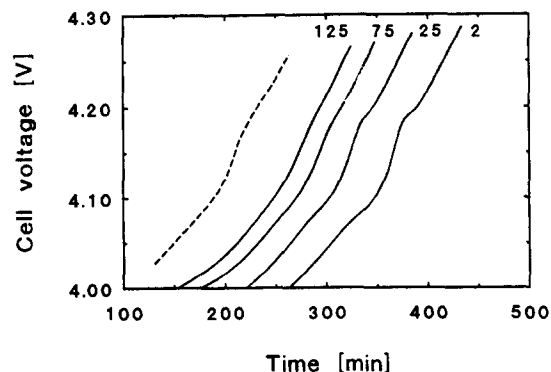


Fig. 3. Part of the 0.2 mA charge curves for different cycles as indicated. The dashed line is a smoothed version of the curve for cycle 2, simulating the effect of increased polarization.

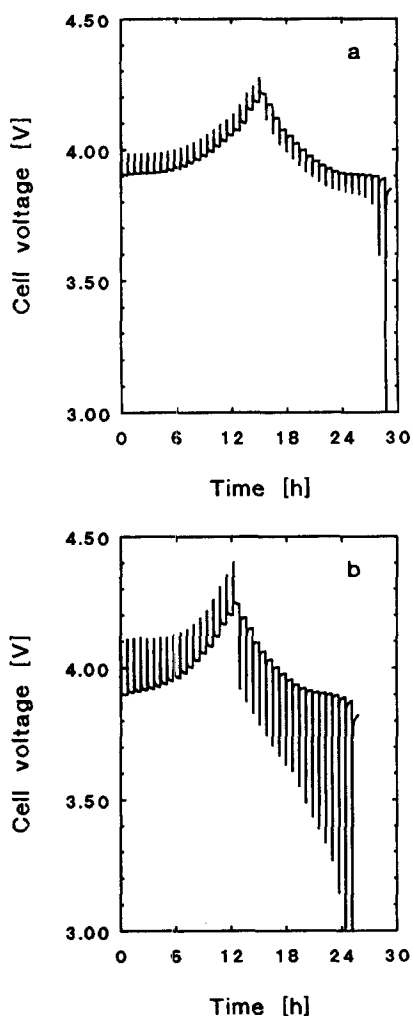


Fig. 2. Relaxation of cell voltage after 4 min/1 mA current pulses for (a) a fresh cell and (b) after 100 cycles between 3.3 and 4.3 V.

same cell after 100 cycles. Polarization increases considerably, especially on discharge. Most of the relaxation takes place within a few minutes. The remaining relaxation takes more than 30 min. Given the particle size and diffusion coefficient [3], a relaxation time in

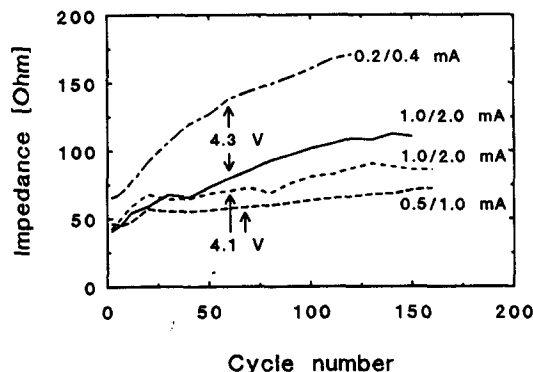


Fig. 4. Change in impedance calculated from the relaxation in 5 min from 4.1 or 4.3 V for the test cells of Fig. 1.

the order of seconds or minutes is expected. The other, larger time constant can be explained by diffusion between Li_xCoO_2 particles of different compositions.

The amount of active material remains nearly constant, as can be seen from the charging time between 4.05 and 4.25 V (cf. Fig. 3). From cycles 2 to 125 the total capacity is reduced by nearly 30%, but the capacity between 4.05 and 4.25 V by only 5%. The feature around 4.15 V is related to an order–disorder transition in Li_xCoO_2 near $x=0.5$ [4]. Fig. 3 shows that this feature gradually disappears with increasing cycle number, which suggests disintegration of the Li_xCoO_2 structure. However, smoothing would also be observed if polarization would vary over the cathode. This is illustrated by the dashed curve which has been obtained by convolution of the curve for cycle 2 with a block of 60 mV width.

The increasing polarization may be caused by disintegration of Li_xCoO_2 grains or deterioration of the contacts between the grains as a result of volume changes on charge and discharge. A large current density produces the largest strain within grains, a low current density the largest change in composition. Increased polarization may also be the result of the formation of a polymer layer on the Li_xCoO_2 grains [5]. This reaction is promoted by high voltages.

Fig. 4 shows the changes in impedance (polarization/current) for cells cycled at different currents between 3.3 and 4.1 V or 4.3 V. Clearly, the maximum voltage is important. The large effect at 0.2/0.4 mA can be explained by the long duration of each cycle. In a similar plot of impedance versus time the results at 4.3 V coincide. Hence, we conclude that the reaction with the electrolyte is the most likely explanation for the observed degradation.

4. Conclusions

The cycle life of Li/Li_xCoO₂ batteries with PC-based electrolyte increases when current density and maximum operating voltage are reduced. A lower current density merely masks the polarization increase. A lower operating voltage actually reduces the increase in polarization. Optimum results are obtained if the maximum voltage is limited to 4.1 V.

It seems unlikely that the order/disorder transition of Li_xCoO₂ around 4.15 V limits the practical voltage of Li/Li_xCoO₂ batteries. The apparent disintegration of the Li_xCoO₂ structure can be explained by polarization differences within the cathode, probably caused by a reaction between Li_xCoO₂ and the electrolyte. Further work is needed to develop an electrolyte stable at higher voltages.

References

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