

Rechargeable LiCoO_2 in inorganic electrolyte solution

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Abstract

The charge/discharge reaction of LiCoO_2 electrode in an inorganic electrolyte solution consisting mainly of LiAlCl_4 and SO_2 has been studied. Three different phases of lithium intercalation/deintercalation were found in voltammograms. Cycling behaviour of LiCoO_2 electrode shows an increasing electronic resistance in the LiCoO_2 bulk. The studied electrode/electrolyte combination is capable to withstand overcharging up to 5 V versus Li/Li^+ without any capacity decrease.

Introduction

LiCoO_2 is one of the most promising compounds for the positive electrode of rechargeable lithium batteries. Its high theoretical gravimetric energy density of 1070 W h/kg and a cell voltage of 4 V make the development of a rechargeable $\text{Li/Li}_x\text{CoO}_2$ system very attractive. But the benefit of high operating potential has detrimental effects on system stability. Only few electrolyte solutions are capable to resist oxidation reactions. Organic solutions such as alkyl ester carbonates with LiAsF_6 were found to be suitable for charging up to 4.3 V. It was reported that higher charging causes formation of irreversible Li_xCoO_2 phases and accelerate solvent oxidation [1].

Experimental

In order to investigate the performance and the cycle life of Li_xCoO_2 electrodes we used an inorganic electrolyte, consisting mainly of LiAlCl_4 and SO_2 . The performance of this electrolyte is described in more detail in ref. 2. All experiments were carried out at room temperature in a glove box with argon atmosphere. Argon gas was circulated over zeolite and P_2O_5 . A three-electrode glass cell with Li as counter and reference electrodes was used for the electrochemical experiments. The LiCoO_2 discs with a diameter of 9 mm and an average surface area of 1.3 cm^2 were prepared. Cyclic voltammetry was performed in the potential region from 3.5 to 4.5 V versus Li/Li^+ with a sweep rate of 0.05 mV/sec (Fig. 1). The three-dimensional figures were constructed by fitting a grid to the voltammograms of 16 cycles (Fig. 2). Each cycle was moved by an equal distance in the z-direction to gain a computer-based volume model. Figures 3 and 4 are different views of the same data base as Fig. 2.

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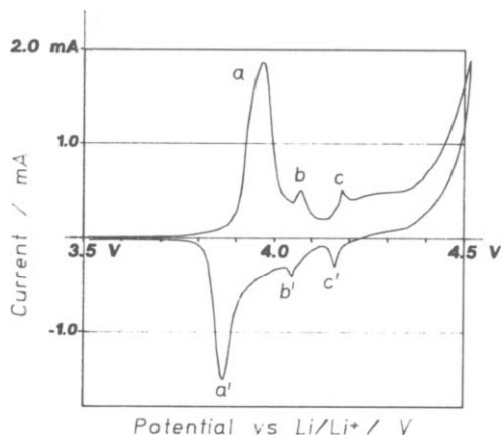


Fig. 1. Cyclic voltammogram of LiCoO_2 electrode C4/384. First cycle.

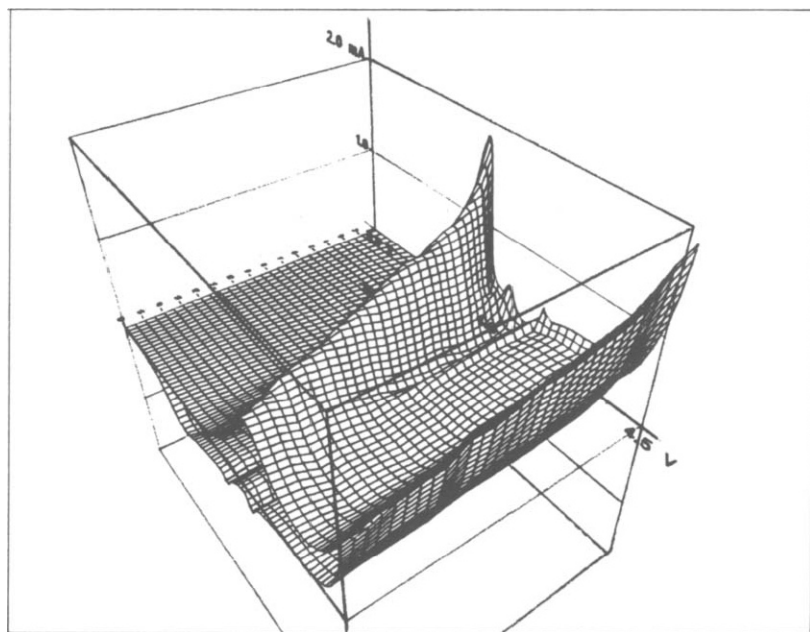


Fig. 2. Three-dimensional view of cyclic voltammograms of LiCoO_2 electrode C4/384. Cycle 1 to 16 in z-direction.

Results and discussion

According to experiences in organic electrolytes, the LiCoO_2 charge/discharge reaction in inorganic electrolyte is divided into three regions [1]. As shown in the cyclic voltammogram of Fig. 1, most of the Li exchange is performed in peak (a). The Li intercalation process is highly reversible. Nevertheless, with further cycling, peak (a) is flattened and dislocated to a more positive potential (Fig. 2). The corresponding

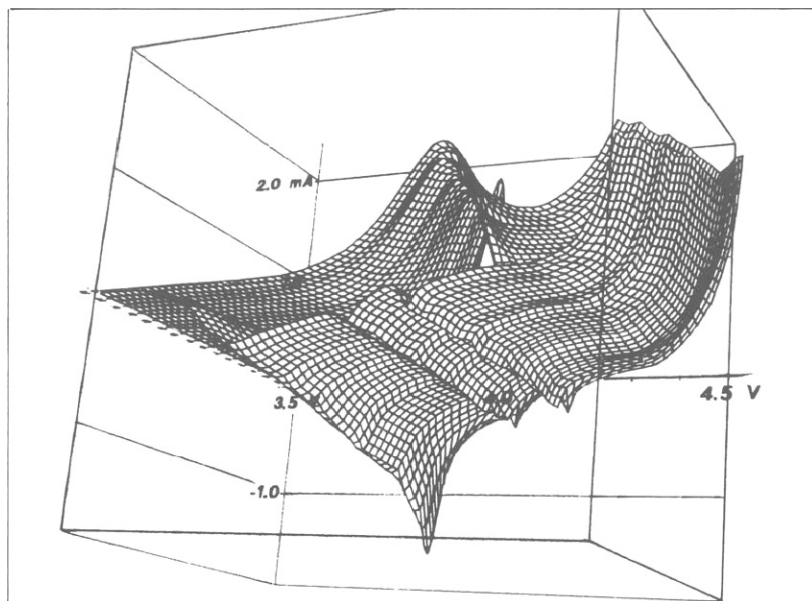


Fig. 3. Three-dimensional view of cyclic voltammograms of LiCoO_2 electrode C4/348; peaks (b') and (c') remain unchanged with cycling.

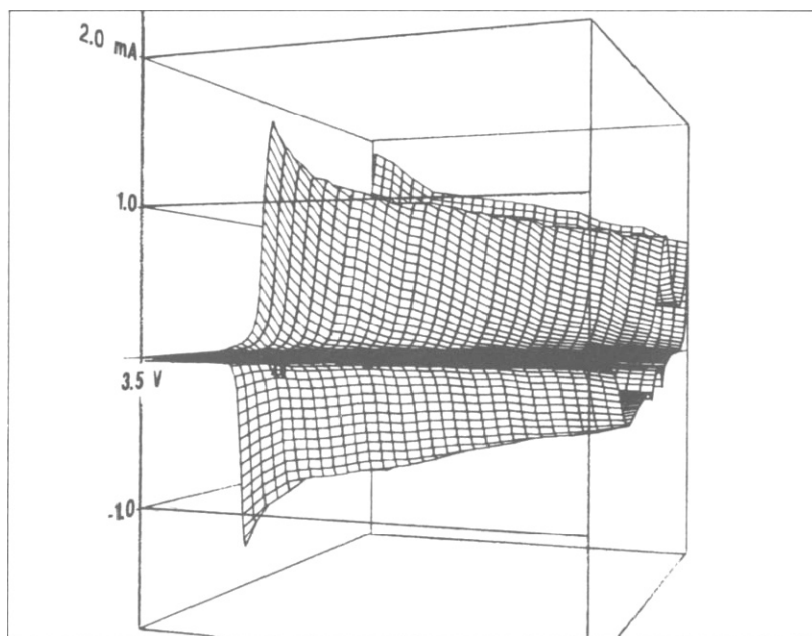


Fig. 4. Three-dimensional view of cyclic voltammograms of LiCoO_2 electrode C4/348; with ongoing cycling peak (a)/(a') becomes flatter.

peak (a') also becomes flatter, but its maximum shifts only about 50 mV to a more negative potential (see also Fig. 4). With ongoing cycling, peak (a) overlaps peaks (b) and (c). According to observations on $\text{Li}_x\text{Mn}_2\text{O}_4$ [3] this behaviour of peak (a) seems to be the result of increasing electronic resistance in the Li_xCoO_2 layer. The different dislocation of peaks (a) and (a') can be understood as the result of the interaction of Li_xCoO_2 electronic conductivity and Li content.

As shown in Fig. 3 peaks (b') and (c') do not change shape nor locations. Even during additional 100 cycles, peaks (b') and (c') remained unchanged.

At potentials more positive than 4.2 V versus Li/Li^+ , chlorine is evolved in a side reaction [4], the amount of chlorine depends on the manufacturing process. As an example, compared with electrode C4/384 (Fig. 1), electrode C4/356 of Fig. 5 shows a much lower chlorine evolution current. This side reaction enables overcharging of $\text{Li}/\text{Li}_x\text{CoO}_2$ batteries. In the studied electrode/electrolyte combination, overcharging up to 5 V causes no extra capacity loss compared with charging up to 4.2 V. In overcharge condition the chlorine will react with metallic Li at the negative electrode to LiCl . To complete the overcharge reaction, LiCl dissolves in the electrolyte and rebuilds a LiAlCl_4 complex with the AlCl_3 produced by the chlorine evolution reaction.

Decay of discharge capacity during potentiodynamic cycling of another electrode sample is shown in Fig. 6. Capacity data were obtained from integrating the area of

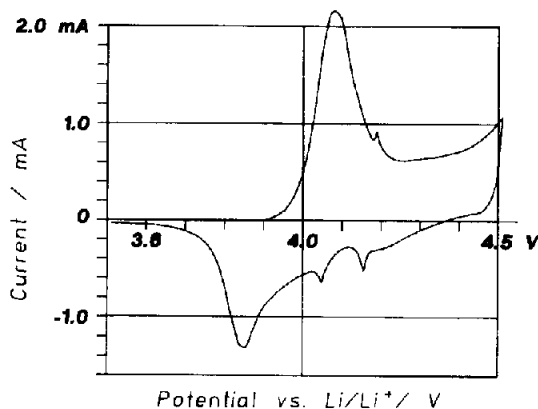


Fig. 5. Cyclic voltammogram of LiCoO_2 electrode C4/356. First cycle.

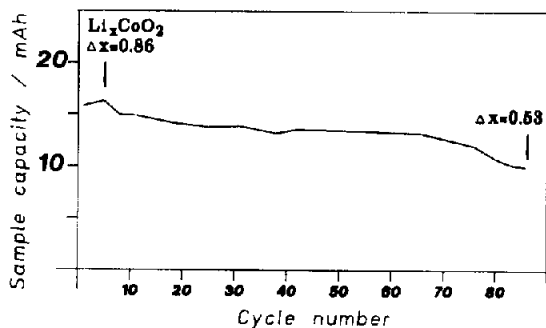


Fig. 6. Capacity of LiCoO_2 electrode C4/163 as a function of cycle number; potentiodynamic cycling: from 3.5 to 4.5 V vs. Li/Li^+ , sweep rate: 0.1 mV/sec.

cathodic current in voltammogram plots. Cycling was performed from 3.5 up to 4.5 V versus Li/Li⁺ with a sweep rate of 0.1 mV/sec.

In the case of an increasing internal resistance, discharging the electrode within a fixed time (≈ 2.8 h) should result in the observed decay of capacity ($\approx 0.3\%$ /cycle). As a matter of fact, with a slower discharge rate we observed a larger remaining capacity.

Conclusions

In half-cell experiments the LiCoO₂ electrode in inorganic electrolyte (LiAlCl₄ and SO₂) has large capacity and rate capability. Improving the internal electronic conductivity of the active layer should improve cycle stability. The studied electrode/electrolyte system could be charged up to 5 V, resulting in chlorine evolution. Future work will lower the overcharge reaction to minimize self-discharge and optimize cycle stability.

References

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