

High voltage aging of LiCoO₂

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LiCoO₂ is known to yield a specific capacity of 137 mAh/g corresponding to a change in the lithium stoichiometry of $\Delta x=0.5$ during the charge/discharge operations. The typical working voltage is between 3.0 V (discharge LiCoO₂) and 4.2 V (charged Li_{0.5}CoO₂). Driving the charging voltage higher than 4.2 V has been considered by several authors as a mean to increase the specific capacity of the electrode [1]. High voltage studies were also motivated by the characterization of the structure changes in heavily de-lithiated cobalt oxide [2, 3].

However, our recent observation of electrolyte oxidation, lithium chemical back intercalation and irreversible phase transformations during thermal aging of Li_{0.5}CoO₂ suggests some adverse effects on the electrode stability should take place upon charging at high voltage [4].

In this study, a Li/1M LiClO₄-PC/LiCoO₂ half-cell was cycled between 3.0 V and 4.2 V for several cycles. Higher voltages were applied in a stepwise manner from 4.2 to 4.7 V by 0,05V increments. The voltage was applied for one hour, followed by 1-hour relaxation. The current in the cell was monitored during each step.

Figure-1 shows the current vs. $t^{-1/2}$ traces at different applied voltages for the short times ($t < 120$ s) of charging. Their linearity may suggest a diffusion-controlled mechanism during lithium de-intercalation [5]. A change in the curves slope is observed, which could result either from a change in the Li chemical diffusion coefficient or from that of the electrode/electrolyte interfacial characteristics.

Figure-2 compares the charge/discharge profiles of cells charged to 4.2 V and the one charged up to 4.7 V, at the end of the incremental charging process. It clearly shows an increased polarization in the cell and a decrease in the cycle capacity. The cell polarization may result from the electrolyte decomposition and/or from changes in the electrode/electrolyte interface. The capacity loss should also relate to the above electrolyte and interfacial effects or to some high voltage induced irreversible changes in electrode crystal structure.

The thermodynamics and the kinetics of such high voltage aging are currently under investigation.

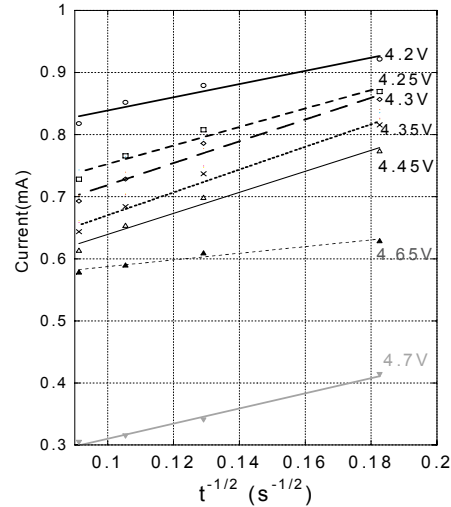


Fig.1: Current vs. $t^{-1/2}$ curves at different voltages applied to the Li_xCoO₂ electrode

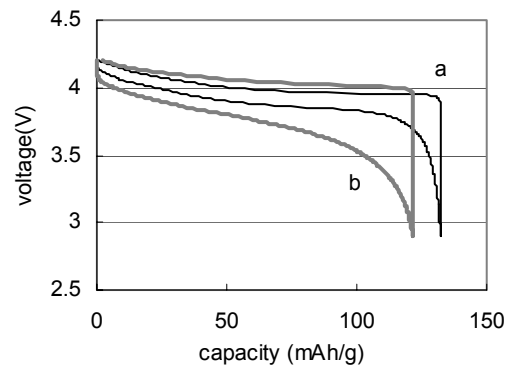


Fig.2: Charge/discharge profiles under C/5-rate of the Li/Li_xCoO₂ half-cells after applying 4.2 V (a) and 4.7 V (b) as the charge upper limit voltage for 1 hour.

[1] Y. Jang et al. J. Electrochem. Soc. 149(2002)1442

[2] L. Seguin et al. J. Power Sources 81-82(1999)604

[3] Z. Chen et al. Proc. 202nd Meet. Electrochem. Soc., Salt Lake City, Oct. 20-24, 2002, Abst. #104

[4] Y. Ozawa et al. This proceeding.

[5] W. Weppner et al. Ann. Rev. Mat. Sci. 8(1978)269