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High-Voltage Cycling Behavior of Thin-Film $LiCoO_2$ Cathodes

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Utilization of a Li_xCoO_2 cathode is typically limited to x = 0.5 (corresponding to ~4.2 V vs. Li), which has been attributed to mechanical failure associated with the large change in c parameter for $x < 0.5$ [1]. It has been suggested that the electrochemical grinding above 4.2 V results in capacity loss as well as cobalt dissolution in non-aqueous liquid electrolytes [2]. Oxidative decomposition of the liquid electrolyte on the electrode surface at high voltages above 4.2 V also degrades the battery performance [3]. To increase the capacity and energy density utilization, efforts have been made to enhance the cycling stability to voltages above 4.2 V by surface treatment or doping of $LiCoO_2$ powders [3,4].

We show that thin-film $LiCoO_2$ cathodes having grains of 0.2-0.3 µm size combined with an amorphous lithium phosphorous oxynitride electrolyte, known as Lipon [5], exhibit excellent capacity when charged up to 4.4 V, unlike conventional composite powder cathodes (see Fig. 1). As Lipon films are electrochemically stable up to 5.5 V at room temperature [6], capacity fade due to electrolyte decomposition is avoided in the solid-state thin-film batteries used in this study. The high-voltage cycling stability of thin-film $LiCoO_2$ cathodes is attributed to mechanical stability associated with a small grain size. No evidence of grain fracture was detected by direct observation of the cycled thin-film cathodes by transmission electron microscopy.

By extending the charge cutoff voltage from 4.2 to 4.5 V, the utilization of energy density increased by 38% at 0.1 mA/cm^2 corresponding to 1.4C rate (1C = 140 mA/g). The trade-off is a more rapid increase in cell resistance when charged above 4.4 V, which can be attributed to the onset of phase transition at >4.4 V (see Fig. 2). The phase transition occurring at ~4.55 V is accompanied by large change (~9%) in the c parameter [7].

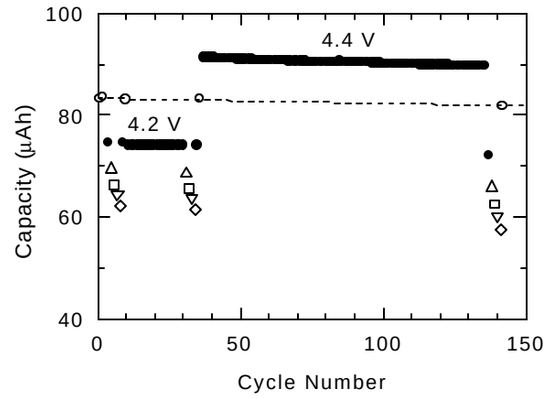

Figure 1. Discharge capacities with charge cutoff voltages of 4.2 and 4.4 V. The discharge cutoff voltage was fixed at 3.0 V. All the cycles represented by the symbol ● were performed at 0.1 mA/cm^2. The cells were intermittently cycled at different current densities between 3.0 and 4.2 V. The symbols ○, Δ, □, ∇, and ◇ correspond to 0.005, 0.3, 0.5, 0.7, and 1 mA/cm^2, respectively.

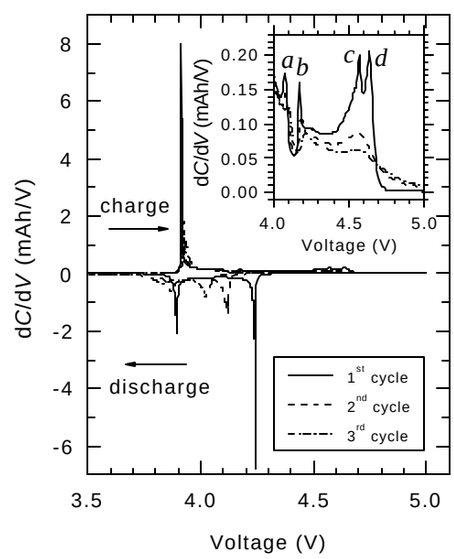

Figure 2. Differential capacity plots during charge and discharge between 3.0 and 5.0 V. All the cycles were performed at 0.01 mA/cm^2 at 25°C.

References

1. T. Ohzuku, A Ueda, M. Nagayama, Y. Iwakoshi, and H. Komori, *Electrochim. Acta*, **38**, 1159 (1993).
2. G. G. Amatucci, J. M. Tarascon, and L. C. Klein, *Solid State Ionics*, **83**, 167 (1996).
3. E. Endo, T. Yasuda, A. Kita, K. Yamaura, and K. Sekai, *J. Electrochem. Soc.*, **147**, 1291 (2000).
4. J. Cho, C.-S. Kim, and S.-I. Yoo, *Electrochem. Solid-State Lett.*, **3**, 362 (2000).
5. J. B. Bates, N. J. Dudney, G. R. Gruzalski, R. A. Zuhr, A. Choudhury, C. F. Luck, and J. D. Robertson, *Solid State Ionics*, **53-56**, 647 (1992).
6. X. Yu, J. B. Bates, G. E. Jellison, Jr., and F. X. Hart, *J. Electrochem. Soc.*, **144**, 524 (1997).
7. G. G. Amatucci, J. M. Tarascon, and L. C. Klein, *J. Electrochem. Soc.*, **143**, 1114 (1996).

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