

# Effect of Li Ordering on Li Diffusion and Cycling Behavior of Thin-Film $\text{LiCoO}_2$ Cathodes

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Extraction of Li from  $\text{LiCoO}_2$  occurs via several phase transitions. In  $\text{Li}_x\text{CoO}_2$ , two hexagonal phases coexist for  $0.75 \leq x \leq 0.93$  [1]. At compositions near  $\text{Li}_{0.5}\text{CoO}_2$ , Li ions are ordered in rows separated by rows of vacancies within the Li layers, which is accompanied by a lattice distortion to a monoclinic symmetry [1,2]. Reversible delithiation in commercial  $\text{Li}_x\text{CoO}_2$  batteries is typically limited to  $x \sim 0.5$  (corresponding to  $\sim 4.2$  V vs. Li) [3]. It was previously suggested that the hexagonal  $\leftrightarrow$  monoclinic phase transition is the major cause of structural degradation of  $\text{Li}_x\text{CoO}_2$  [4].

This paper focuses on the effect of Li ordering at  $x \sim 0.5$  on the Li diffusion and the cyclability of  $\text{Li}_x\text{CoO}_2$  cathodes. To measure the diffusion coefficient of Li with well-defined diffusion geometry, we employed solid-state thin-film Li batteries using the amorphous lithium phosphorus oxynitride (Lipon) electrolyte developed at ORNL [5]. In order to elucidate the effect of Li ordering, we prepared  $\text{Li}_x\text{CoO}_2$  cathodes showing different degrees of Li ordering near  $x \sim 0.5$ .

The diffusion coefficients were determined by the potentiostatic intermittent titration technique (PITT) in the composition range of  $0.45 < x < 0.7$ , where  $\text{Li}_x\text{CoO}_2$  exists as a single phase having either a hexagonal or a monoclinic structure [6]. The self diffusion coefficient of Li has a minimum at  $x \sim 0.5$ , attributed to a higher activation energy associated with Li jumps in the ordered phase [7]. The minimum becomes more pronounced as the degree of Li ordering increases (see Fig. 1). Cells with the hexagonal  $\leftrightarrow$  monoclinic phase transition exhibited excellent cyclability when charged up to 4.35 V (see Fig. 2). The fact that there is no deterioration upon cycling across the phase boundaries near  $x \sim 0.5$  may be explained by small strain associated with the phase transition.

## References

1. J. N. Reimers and J. R. Dahn, *J. Electrochem. Soc.*, **139**, 2091 (1992).
2. T. Ohzuku and A. Ueda, *J. Electrochem. Soc.*, **141**, 2972 (1994).
3. G. G. Amatucci, J. M. Tarascon, and L. C. Klein, *Solid State Ionics*, **83**, 167 (1996).
4. J. Cho, C.-S. Kim, and S.-I. Yoo, *Electrochem. Solid-State Lett.*, **3**, 362 (2000).
5. J. B. Bates, N. J. Dudney, and K. A. Weatherspoon, U.S. Pat. 5, 561,004 (1996).
6. Y.-I. Jang, B. J. Neudecker, and N. J. Dudney, *Electrochem. Solid-State Lett.*, **4** (2001).
7. A. Van der Ven and G. Ceder, *Electrochem. Solid-State Lett.*, **3**, 301 (2000).

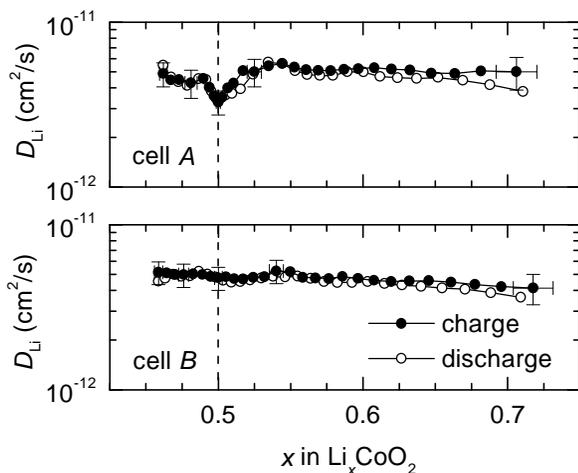


Fig. 1. Self diffusion coefficients of Li ( $D_{\text{Li}}$ ) obtained by PITT at 25°C. The degree of Li ordering in the cathode of cell A is higher than that of cell B.

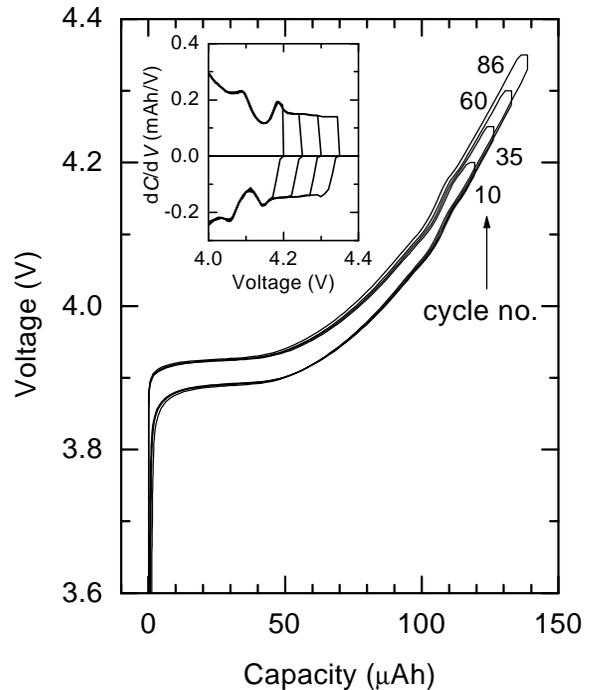


Fig. 2. Charge-discharge curves with the various charge cutoff voltages of 4.2, 4.25, 4.3, and 4.35 V. The discharge cutoff voltage was fixed at 3.0 V. Inset shows the corresponding differential capacities. All the cycles were performed at  $0.1 \text{ mA/cm}^2$  at 25°C.

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