

Application of Fluorine-containing Solvents to LiCoO₂ Cathode in High Voltage Operation

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We applied fluorine-containing solvents (FCSs) to an electrolyte for lithium (Li)-ion batteries with a cobalt oxide (LiCoO₂) cathode to enhance the upper voltage limit and investigated its electrochemical properties in a proposed FCS-based electrolyte. FCSs were expected to have high oxidation resistance by introducing electron withdrawing fluorine atoms. A test cell containing a FCS-based electrolyte exhibited high and stable discharge capacity in 30 cycles even with a high upper cutoff voltage of 4.5 V when compared with a cell containing a conventional electrolyte. This improvement in the cycle performance was confirmed by an electrochemical impedance measurement. We found that the FCS-based electrolyte provides a favorable solid electrolyte interface (SEI) at the LiCoO₂ cathode, leading to reversible charge-discharge behavior of the cathode.

Key Words : Lithium-ion Battery, Fluoroethylene Carbonate, LiCoO₂, High Voltage

1 Introduction

A lithium Li-ion battery is being developed as a large-sized power supply in a hybrid electric vehicle (HEV) as well as “pure” electric vehicles (EV). Therefore when their energy and power densities are increased, the safety improvement of Li-ion batteries becomes crucial. Conventional Li-ion batteries with a combustible organic solvent electrolyte suffer from the risk of ignition caused by a short circuit or overcharge. Consequently, a safe system must be designed to solve this problem.

Recently, a nonflammable fluorine-containing solvent (FCS) has attracted attention since it ensures the safety of batteries.¹⁻⁶⁾ Furthermore, since it may expand the operating cell voltage due to its high oxidation resistance, it can improve the energy density of Li-ion batteries. McMillan *et al.* reported good cycle performance in their Li-ion battery that contained fluoroethylene carbonate (FEC) with a graphite anode.¹⁾ Choi *et al.* described how FEC as an additive formed an electrochemically stable solid electrolyte interface (SEI) that included LiF and silicon (Si) fluorides on a Si thin-film anode.²⁾ Profatilova *et al.* reported that an electrolyte including FEC enhanced the thermal properties of a lithiated/delithiated graphite anode.³⁾ Although the valuable effects of FCSs such as FEC have been reported in these previous investigations, little has been discovered about the effect of FCSs on cathode performance.

In this work, we investigated the effect of our FCS-based electrolyte on a LiCoO₂ cathode. Since LiCoO₂ has a good cycle performance, it is widely used as a cathode material in current commercial Li-ion batteries. However, its reversible capacity is limited due to the destabiliza-

tion of the structure with excessive deintercalation of Li⁺ ion.⁷⁾ Therefore, many researchers have attempted to expand its operating voltage by coating the LiCoO₂ surface with such inorganic compounds as ZrO₂^{8,9)} and Al₂O₃¹⁰⁾ for surface stabilization. Our proposed attempt here is a different approach to expand the operating voltage: the application of a FCS-based electrolyte to modify the LiCoO₂ surface without the above inorganic coating on the cathode. Our FCS-based electrolyte proposed led to high voltage operation without chemically coating the LiCoO₂ surface.

2 Experimental

Figure 1 shows the molecular structure of 1,1,2,2-tetrafluoro-3-(1,1,2,2-tetrafluoroethoxy)-propane (TFTFEP), synthesized by Daikin Industries, Co.¹¹⁾ The proposed FCS-based electrolyte was a mixture of FEC and TFTFEP in a 1:1 volume ratio and contains a 1.0 mol dm⁻³ Li hexafluorophosphate (LiPF₆). The “conventional” electrolyte as a reference for comparison was a mixture of ethylene carbonate (EC, Kishida Chemical Co.) and dimethyl carbonate (DMC, Kishida Chemical Co.) in a 1:1 volume ratio with the same concentration of LiPF₆. The electrochemical properties of these electrolytes are shown in Table 1.

Electrochemical measurements were performed using a coin-type cell (Hohsen Corp.) that was constituted by LiCoO₂ as a cathode and a Li metal (Honjo Metal Co.) as a counter electrode (Li/LiCoO₂ cell). The composition of the LiCoO₂ cathode was 85 wt.% of LiCoO₂, 7 wt.% of carbon black (CB), and 8 wt.% of polyvinylidene difluoride (PVdF). Celgard 3501 (Celgard Co., made of

Table 1 Electrochemical properties of FCS-based and conventional electrolyte containing 1.0 mol dm⁻³ LiPF₆ at 25 °C.

	Viscosity/mPa s	Ionic conductivity/mS cm ⁻¹
FCS-based	9.44	3.51
Conventional	3.66	11.39

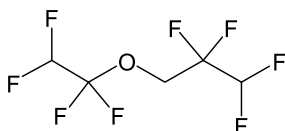


Fig. 1 Molecular structure of 1,1,2,2-Tetrafluoro-3-(1,1,2,2-tetrafluoroethoxy)-propane (TFTFEP).

polypropylene, thickness: 25 µm) was used as a separator. All the assembling processes of the cell were done in a dry room (dew point; below *ca.* -60 °C).

The charge-discharge measurements were performed in a constant current-constant voltage (CC-CV) mode (terminated when the current reduced to 1/10 of the initial value) for charging to 4.2 or 4.5 V with a constant current (CC) mode for discharging to 3.0 V with a BTS2004-W (Nagano Co.) at room temperature. The operating current in CC for charging and discharging was 1.0 C-rate. A frequency response analyzer (Solartron 1255B) coupled with an electrochemical interface (Solartron 1287) was used for the electrochemical impedance measurements. The ac frequency was scanned from 20 kHz to 10 mHz with an amplitude of 10 mV_{p-p}. To achieve an equilibrium state, relaxation time (1 h or longer) was applied after each constant-current polarization.

3 Results and Discussion

Figure 2 shows the cycle performance for Li/LiCoO₂ cells with a FCS-based electrolyte and the conventional electrolyte, where the upper charge cutoff voltage is limited to 4.2 or 4.5 V. The discharge capacity with the FCS-based electrolyte is somewhat lower than that with the conventional electrolyte at a cutoff voltage of 4.2 V due to the relatively lower ionic conductivity of the FCS-based electrolyte (Table 1); this increases the potential loss for the cathode operation, and hence cathode utilization becomes lower than that with the conventional electrolyte.

Significant capacity degradation during cycles is observed with the conventional electrolyte when the upper cutoff voltage is expanded to 4.5 V. This originates from two factors. One is the structure destabilization caused by the phase transition of LiCoO₂. Chen *et al.* reported that the performance of LiCoO₂ cycled in a high voltage range becomes poor by a structure change from the O3 to the H1-3 Phase.¹²⁾ The other is the oxidative decomposition of the solvents in the high voltage range; decomposition products increase the interfacial resistance and degrade the function of the cathode surface.

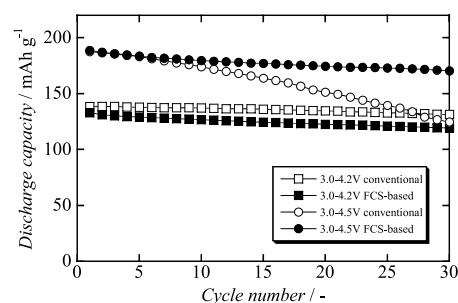


Fig. 2 Cycle performance of Li/LiCoO₂ cell with conventional and FCS-based electrolytes in voltage ranges of 3.0-4.2 and 3.0-4.5 V.

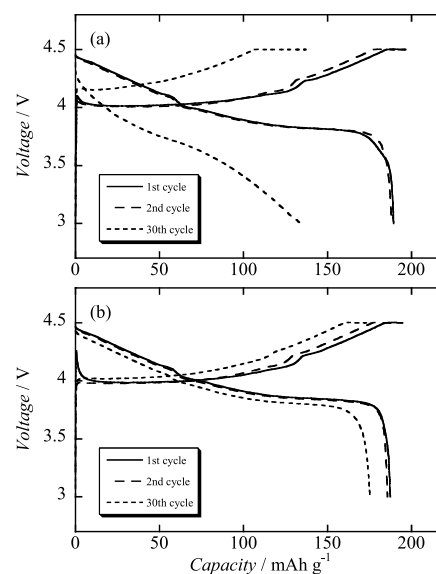


Fig. 3 Charge-discharge curves for (a) conventional and (b) FCS-based electrolytes in Li/LiCoO₂ cells at 1st, 2nd and 30th cycles. These curves were recorded at a rate of 1.0 C in cell voltage range between 3.0 and 4.5 V.

In marked contrast to the reference system, the present FCS system provides a high and stable discharge capacity in 30 cycles even with a 4.5 V cutoff. This suggests that the SEI film originated from the FCS-based electrolyte would be electrochemically stable. Interestingly, this film formation appears to inhibit or stabilize the undesirable phase transition of the LiCoO₂ and to protect the cathode against further oxidative decomposition of the electrolyte at the electrode surface.

The charge-discharge curves of the Li/LiCoO₂ cells in a voltage range of 3.0-4.5 V are shown in Fig. 3. Polarization increases and a clear discharge plateau disappears with cycling in the conventional electrolyte, probably due to the destabilization of the electrode structure [Fig. 3(a)]. On the other hand, stable charge-discharge curves are observed even at the 30th cycle in the FCS-based electrolyte [Fig. 3(b)]. This suggests that the polarization resistance is stable with cycling and the cathode reaction remains reversible even with a high cutoff voltage of 4.5 V in the FCS-based electrolyte. After these cycling tests the appearance of a Li counter

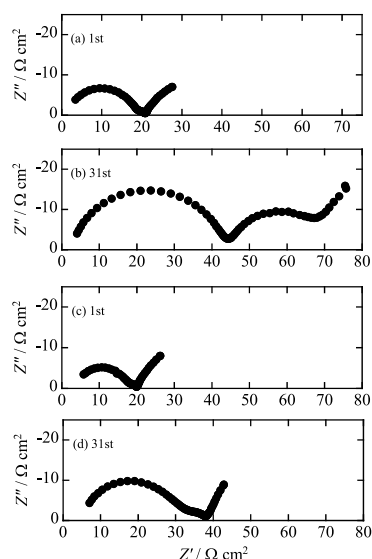


Fig. 4 Nyquist plots of LiCoO₂ cathode in (a, b) conventional and (c, d) FCS-based electrolytes at 1st and 31st charge states at 4.5 V.

electrode almost looked unchanged in both the tested electrolytes at 4.2 and 4.5 V. Therefore, the influence of the counter electrode on the cell performance is negligible. To confirm the difference in the cathode interface in the tested electrolytes, we performed electrochemical impedance measurements.

Figure 4 shows typical Nyquist plots for the Li/LiCoO₂ cells with both electrolytes. Each impedance response is measured at a full charge state at 4.5 V. A straight line with a 45° slope in a low frequency range relates to the finite-length Warburg impedance for solid-state Li⁺ ion diffusion. Two overlapping semicircles are observed in the high and middle frequency regions. The semicircle component in the high frequency region would include not only contact resistances between particles but also a charge-transfer resistance coupled with a double-layer capacitance of the electrode.¹³⁻¹⁶⁾ On the other hand, the other, smaller semicircle, which is quite small except for (b), in the middle frequency region is present only at high voltage operation (3.0-4.5 V) and is not observed at a charge cutoff voltage of 4.2 V (data not shown here). Judging from these facts, this semicircle component would be assigned to the surface film resistance formed on the LiCoO₂ cathode.

Characteristic changes in these impedance spectra with cycling are observed in the semicircle components. As for the conventional electrolyte, the semicircle in the high frequency region, which becomes much larger in 31 cycles [Figs. 4(a) and (b)], is also much larger than that observed in the FCS-based electrolyte at the same 31st cycle [Fig. 4(d)]. This significant increase in the conventional electrolyte would be ascribed to the structure degradation of the LiCoO₂ cathode in 30 cycles. In contrast, an increase in this resistance component is not significant in the FCS-based electrolyte, suggesting that this electrolyte is effective in preventing the structure degradation and maintaining the cathode reversibility even if

the phase transition occurs.

Moreover, the other semicircle component in the middle frequency region, attributed to a surface film formed on the cathode, increases drastically in the conventional electrolyte, and no significant increase is observed in the FCS-based system. These results correlate well with the above results in Fig. 3; the significant increase in the polarization resistance observed in the charge-discharge curves with cycling in the conventional electrolyte is attributed to the remarkable increases in these two impedance components.

From the above results and discussion, the proposed FCS-based electrolyte provides an electrochemically stable surface film on a LiCoO₂ cathode and significantly improves the cycle performance under a high-voltage condition, suggesting that the electrolyte would probably drastically improve the energy density of Li-ion batteries based on a LiCoO₂ cathode.

4 Conclusion

The electrochemical behavior of Li/LiCoO₂ cells containing a FCS-based electrolyte was investigated. Even when the charge cutoff voltage was increased to 4.5 V, a good cycle performance was obtained in the proposed electrolyte in 30 cycles, and degradation behavior of the cell by structure destabilization of a LiCoO₂ cathode was observed for the conventional electrolyte. The FCS-based electrolyte inhibits an increase in the polarization resistance with cycling, suggesting its protection effect against further oxidative decomposition of the electrolyte/electrode in high voltage. We consider such a FCS-based electrolyte a promising system under a high-voltage condition.

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References

- 1) R. McMillan, H. Sleg, Z. X. Shu, and W. Wang, *J. Power Sources*, **81**, 20 (1999).
- 2) N.-S. Choi, K. H. Yew, K. Y. Lee, M. Sung, H. Kim, and S.-S. Kim, *J. Power Sources*, **161**, 1254 (2006).
- 3) I. A. Profatlova, S.-S. Kim, and N.-S. Choi, *Electrochim. Acta*, **54**, 4445 (2009).
- 4) T. Achiha, T. Nakajima, Y. Ohzawa, M. Koh, A. Yamauchi, M. Kagawa, and H. Aoyama, *J. Electrochem. Soc.*, **156**, A483 (2009).
- 5) J. Yamaki, S. Yamami, T. Doi, and S. Okada, *Electrochem. Soc.*, **602**, 263 (2006).
- 6) K. Naoi, E. Iwama, N. Ogihara, Y. Nakamura, H. Segawa, and Y. Ino, *J. Electrochem. Soc.*, **156**, A272 (2009).
- 7) J. Cho and G. Kim, *Electrochem. Solid-State Lett.*, **2**, 253 (1999).
- 8) J. Cho, Y. J. Kim, T.-J. Kim, and B. Park, *Angew. Chem. Int. Ed.*, **40**, 3367 (2001).
- 9) K. Y. Chung, W.-S. Yoon, J. McBreen, X.-Q. Yang, S. H. Oh, H. C. Shin, W. I. Cho, and B. W. Cho, *J. Power*

- Sources*, **174**, 619 (2007).
- 10) Z. Chen and J. R. Dahn, *Electrochem. Solid-State Lett.*, **5**, A213 (2002).
 - 11) PCT/JP2009/060694.
 - 12) Z. Chen and J. R. Dahn, *Electrochim. Acta*, **49**, 1079 (2004).
 - 13) M. Morita, O. Yamada, and M. Ishikawa, *J. Power Sources*, **81**, 425 (1999).
 - 14) D. Aurbach, B. Markovsky, M. D. Levi, E. Levi, A. Schechter, M. Moshkovich, and Y. Cohen, *J. Power Sources*, **81**, 95 (1999).
 - 15) O. Yamada, M. Ishikawa, and M. Morita, *Electrochim. Acta*, **45**, 2197 (2000).
 - 16) M. Morita, T. Nakagawa, O. Yamada, N. Yoshimoto, and M. Ishikawa, *J. Power Sources*, **97**, 354 (2001).