Highly reversible lithium metal secondary battery using a room temperature ionic liquid/lithium salt mixture and a surface-coated cathode active material

Shiro Seki,*[ac] Yo Kobayashi,[a] Hajime Miyashiro,[a] Yasutaka Ohno,[b] Akira Usami,[a] Yuichi Mita,[a] Masayoshi Watanabe[c] and Nobuyuki Terada[a]

Received (in Cambridge, UK) 17th October 2005, Accepted 23rd November 2005
First published as an Advance Article on the web 15th December 2005
DOI: 10.1039/b514681j

For the purpose of realizing high-voltage, high-capacity, long-life and safe rechargeable batteries, a lithium secondary battery that uses high-voltage stable ZrO_2-coated $LiCoO_2$ cathode powder and a nonvolatile high-safety room temperature ionic liquid was fabricated.

Research and development of high-energy-density, long-life lithium secondary batteries as large-scale energy storage devices, for example, electric vehicles, has progressed.[1] Well-known conventional lithium ion secondary batteries contain a nonaqueous organic solvent (*e.g.*, ethylene carbonate, propylene carbonate) as an electrolyte together with a separator and lithium salt. Aiming at the realization of large-scale batteries, the volatility and inflammability of organic solvents are serious problems from the viewpoint of safety. Therefore, all-solid-state batteries using a polymer electrolyte[2] or an inorganic electrolyte[3] have been investigated.

Recently, room temperature ionic liquids (RTILs, molten salts) have received increasing attention as new solvents. RTILs consist of only cations and anions and have many attractive properties, for example, nonflammability, nonvolatility, thermal stability, and high ionic conductivity owing to the high ionic concentrations in their liquid solution.[4] Moreover, polymerization of monomers in RTILs can be realized, to obtain homogeneous highly ion-conductive polymer electrolyte films.[5–7] Sakaebe and Matsumoto, and Howlett *et al.* have reported on metallic lithium anode lithium secondary batteries consisting of RTILs (*N*-methyl-*N*-propylpiperidinium bis(trifluoromethylsulfonyl) imide,[8] *N*-methyl-*N*-alkylpyrrolidinium bis(trifluoromethylsulfonyl) imide[9])/lithium salt mixture as an electrolyte. We have also reported a lithium secondary battery that uses the RTIL (*N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)-ammonium bis(trifluoromethylsulfonyl) imide, DEMETFSI)[10] as an electrolyte, and confirmed its reversible charge–discharge operation of more than 100 cycles.[11] Moreover, Passerini *et al.* reported [cathode (V_2O_5 or $LiFePO_4$) | PEO + RTIL + Li salt | Li metal anode] cells as all-solid-state batteries.[12–14]

On the other hand, in recent days, by covering a cathode surface with a stable inorganic oxide (*e.g.*, Al_2O_3, ZrO_2, or TiO_2), an improvement in capacity retention in the high cathode voltage region (>4.2 V *vs.* Lithium metal anode (V)) has been reported in conventional liquid-type (non-aqueous organic electrolyte solution) lithium secondary batteries.[15–17] In this study, to realize a high-capacity and highly reversible lithium secondary battery that uses RTILs, we applied a ZrO_2 coating on a $LiCoO_2$ cathode surface by using spray coating and examined stability at the cathode | electrolyte interface. A favorable battery design that had both the essential safety of RTILs and an excellent high-voltage performance (high battery capacity) with the ZrO_2-coated $LiCoO_2$ cathode was explored.

ZrO_2-coated $LiCoO_2$ powder was prepared by a spray coating method. A ZrO_2 sol solution was sprayed and dried in a fluidized $LiCoO_2$ powder using a coating machine (Powrex MP-01). The amount of ZrO_2 is 3 wt% based on $LiCoO_2$. The obtained ZrO_2-coated $LiCoO_2$ powder was annealed at 823 K for 15 h under an O_2 flow condition. The forms of the powder after coating were confirmed by SEM, TEM and XRD analysis. Details of the preparation have been reported elsewhere.[17] The characteristics of the battery were examined using [$LiCoO_2$ (noncoated or ZrO_2-coated) cathode sheet | RTIL/Li salt | lithium metal anode] cells. The cathode sheet consisted of $LiCoO_2$ (85 wt%), acetylene black (9 wt%, Denka) and PVDF binder (6 wt%, Kureha Chemical). DEMETFSI (purchased from Kanto Kagaku) was used as the RTIL.[10] Lithium bis(trifluoromethanesulfonyl) imide (LiTFSI, Kishida Chemical) was used as the electrolyte salt (LiTFSI concentration of 0.32 mol kg^{-1}, molar ratio of DEMETFSI/LiTFSI is 88/12). The cathode sheet, polypropylene separator, DEMETFSI/LiTFSI electrolyte and lithium metal anode were encapsulated into 2032-type coin cells in a dry-argon-filled glove box ($[O_2] < 0.4$ ppm, $[H_2O] < 0.1$ ppm, Miwa MFG Co., Ltd.). For optimum penetration of the electrolyte into the pressed cathode sheet, the prepared cells were thermally aged at 333 K for 12 h. Charge–discharge tests on the cells were performed at 3.0–4.6 V at a current density of 0.05 mA cm^{-2} (constant current charge–constant current discharge, HJ-101M6, Hokuto Denko). All measurements were performed at room temperature (approximately 298 K).

Fig. 1 shows the cycle dependencies of the cathode-limited discharge capacity of the [$LiCoO_2$ cathode sheet | RTIL/Li salt | lithium metal anode] cells using non-coated $LiCoO_2$ and ZrO_2-coated $LiCoO_2$. In the first-cycle discharge, noncoated $LiCoO_2$ and ZrO_2-coated $LiCoO_2$ cells showed a discharge capacity of more than 180 mAh g^{-1}, close to the theoretical capacity of Li_xCoO_2 ($0.3 < x < 1$). In the case of the noncoated

---

[a] *Materials Science Research Laboratory, Central Research Institute of Electric Power Industry (CRIEPI), 2-11-1 Iwado-kita, Komae, Tokyo 201-8511, Japan. E-mail: s-seki@criepi.denken.or.jp; Fax: +81-3-3480-3401; Tel: +81-3-3480-2111*
[b] *Electric Power Engineering Systems Company Limited, 2-11-1, Iwado-kita, Komae, Tokyo 201-8511, Japan*
[c] *Department of Chemistry and Biotechnology, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama, Kanagawa 240-8501, Japan*

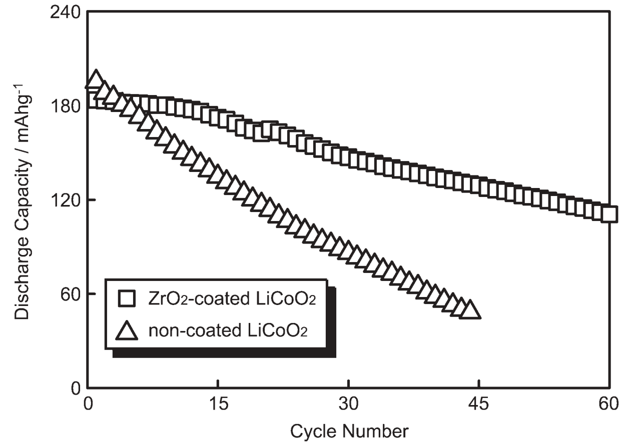

Fig. 1 Relationships between cycle number and cathode-limited discharge capacity for [ZrO_2-coated or non-coated $LiCoO_2$ cathode | DEMETFSI/LiTFSI | lithium anode] cells (voltage range: 4.6–3.0 V *vs.* Li/Li^+, current: 50 μA cm^{-2} = *C*/10, at room temperature).

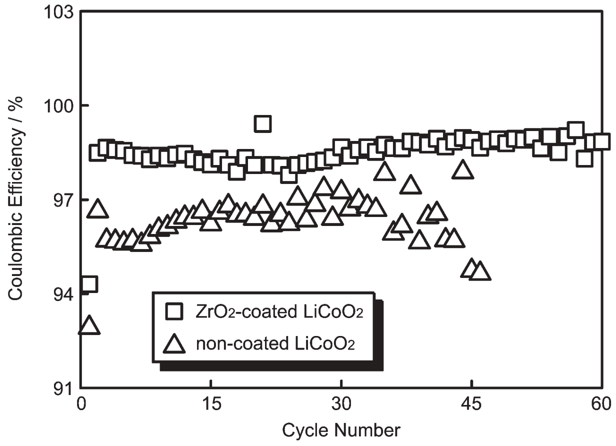

Fig. 2 Relationships between cycle number and Coulombic efficiency for [ZrO_2-coated or non-coated $LiCoO_2$ cathode | DEMETFSI/LiTFSI | lithium anode] cells (voltage range: 4.6–3.0 V *vs.* Li/Li^+, current: 50 μA cm^{-2} = *C*/10, at room temperature).

$LiCoO_2$ cell, the discharge capacity was approximately 85 mAh g^{-1} at 30 cycles, and therefore had linearly decreased by approximately 44% from its initial value. Also, we have confirmed the relationships between the upper-cutoff voltage and relative capacity using noncoated $LiCoO_2$ cells [upper-cutoff voltage = 4.2 and 4.4 V: (30th discharge capacity/1st discharge capacity × 100%) = 92 and 89%, respectively]. Reversibility of the cells was decreased with increasing upper-cutoff voltage. On the other hand, in the case of ZrO_2-coated $LiCoO_2$ cell, the discharge capacity (3.0–4.6 V) was approximately 150 mAh g^{-1} at 30 cycles, which was 82% of its initial value. Compared with noncoated and ZrO_2-coated $LiCoO_2$ cells, the clear effect of capacity retention by ZrO_2 coating could be shown.

Next, Fig. 2 shows the cycle dependencies of the Coulombic efficiency of the [$LiCoO_2$ cathode sheet | RTIL/Li salt | lithium metal anode] cells using non-coated $LiCoO_2$ and ZrO_2-coated $LiCoO_2$. Stable Coulombic efficiencies of 96% and 99%, respectively, for the noncoated $LiCoO_2$ and ZrO_2-coated $LiCoO_2$ cells are shown. The ZrO_2 coating suppressed the loss of charge between the charging and discharging processes. We have also reported the improvement in capacity retention over 4.2 V, with conventional liquid-type (EC/DMC-$LiPF_6$ electrolyte solution) lithium secondary batteries that use the above-mentioned ZrO_2-coated $LiCoO_2$.[17] In addition, we have observed the coating effects of Li_3PO_4 and Al_2O_3 onto the $LiCoO_2$ surface in the case of all-solid-state lithium polymer secondary batteries using a polyether-based polymer electrolyte.[2] C–O bonding or C–C bonding in these electrolytes is more likely to be cleaved by applying high voltages than C–H bonding (average bonding enthalpy; C–O bonding: 360 kJ mol^{-1}, C–C bonding: 348 kJ mol^{-1}, C–H bonding: 436 kJ mol^{-1}). Cathode active materials have high oxidizing abilities in a highly charged state (high voltage state). Since the electrolytes (in this study, DEME cations) contain oxygen atoms, C–O bonding or C–C bonding may cleave. A ZrO_2 coating on the $LiCoO_2$ surface may suppress the oxidizing ability of charged $LiCoO_2$ without affecting the original oxidation–reduction reaction (intercalation–deintercalation of lithium ion) of $LiCoO_2$. Although the effect of a ZrO_2 coating on the cathode surface (high-voltage stability) could also be confirmed in the lithium secondary battery that uses RTIL (high-safety electrolyte solvent) as well as the conventional liquid-type battery, it is still uncertain whether the effect of cathode coating is a phenomenon unique to DEME cations. In future, we will study the degradation and coating mechanism of a lithium secondary battery that uses RTIL in detail by examining batteries that use other RTILs (*e.g.*, imidazolium cations and phosphonium cations).

The authors thank Powrex Co. for their technical support in our research.

Notes and references

1 N. Terada, T. Yanagi, S. Asai, M. Yoshikawa, K. Ohta, N. Nakajima, A. Yanai and N. Arai, *J. Power Sources*, 2001, **100**, 80.
2 S. Seki, Y. Kobayashi, H. Miyashiro, Y. Mita and T. Iwahori, *Chem. Mater.*, 2005, **17**, 2041.
3 J. B. Bates, G. R. Gruzalski, N. J. Dudney, C. F. Luck and X. Yu, *Solid State Ionics*, 1994, **70–71**, 619.
4 A. Noda, K. Hayamizu and M. Watanabe, *J. Phys. Chem. B*, 2001, **105**, 4603.
5 M. A. B. H. Susan, T. Kaneko, A. Noda and M. Watanabe, *J. Am. Chem. Soc.*, 2005, **127**, 4976.
6 S. Seki, M. A. B. H. Susan, T. Kaneko, H. Tokuda, A. Noda and M. Watanabe, *J. Phys. Chem. B*, 2005, **109**, 3886.
7 S. Washiro, M. Yoshizawa, H. Nakajima and H. Ohno, *Polymer*, 2004, **45**, 1577.
8 H. Sakaebe and H. Matsumoto, *Electrochem. Commun.*, 2003, **5**, 594.
9 P. C. Howlett, D. R. MacFarlane and A. F. Hollenkamp, *Electrochem. Solid-State Lett.*, 2004, **7**, A97.
10 T. Sato, T. Maruo, S. Marukane and K. Takagi, *J. Power Sources*, 2004, **138**, 253.
11 S. Seki, Y. Kobayashi, H. Miyashiro, Y. Ohno, Y. Mita, A. Usami, N. Terada and M. Watanabe, *Electrochem. Solid-State Lett.*, 2005, **8**, A577.
12 J.-H. Shin, W. A. Henderson, G. B. Appetecchi, F. Alessandrini and S. Passerini, *Electrochim. Acta*, 2005, **50**, 3859.
13 J.-H. Shin, W. A. Henderson and S. Passerini, *Electrochem. Solid-State Lett.*, 2005, **8**, A125.
14 J.-H. Shin, W. A. Henderson and S. Passerini, *J. Electrochem. Soc.*, 2005, **152**, A978.
15 Z. Chen and J. R. Dahn, *Electrochem. Solid-State Lett.*, 2003, **6**, A221.
16 J. Cho, Y. J. Kim, T-J. Kim and B. Park, *Angew. Chem., Int. Ed.*, 2001, **40**, 3367.
17 H. Miyashiro, A. Yamanaka, M. Tabuchi, S. Seki, M. Nakayama, Y. Ohno, Y. Kobayashi, Y. Mita, A. Usami and M. Wakihara, *J. Electrochem. Soc.*, in press.