

Lithium-ion rechargeable cells with LiCoO₂ and carbon electrodes

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Abstract

Cathodes composed of layered transition metal oxides LiMO₂ (M=Co, Ni) and spinel manganese oxide LiMn₂O₄, carbon anodes, and nonaqueous electrolyte solutions have been investigated with the aim of achieving higher energy density. The lithium-ion rechargeable cell using the LiCoO₂ cathode and the propylene carbonate(PC)-diethyl carbonate (DEC)/LiPF₆ electrolyte solution exhibits excellent characteristics. Furthermore, non-graphitizable carbon such as polyfurfuryl alcohol derived carbon has larger capacity and better cycleability than graphitizable carbon such as coke.

Introduction

Secondary batteries with high energy density are in demand as power sources for smaller, lighter, and better performing portable electronic equipment. In particular, there has been much effort in developing lithium secondary batteries because of their light weight, high voltage, and high energy density [1]. However, there have been some problems caused by the dendritic Li which is formed on the Li metal anode by repeated charging and discharging [2]. In order to resolve these problems, M. Mohri *et al.* [3] have proposed Li-carbon intercalation compounds for the anode material.

Therefore, we have investigated layered transition metal oxides LiMO₂ (M=Co, Ni) and spinel manganese oxide LiMn₂O₄ cathodes, carbon anodes and electrolytes for Li-ion rechargeable cells. These cells have the advantages of high energy density, long cycle life and excellent safety characteristics. However, in order to attain an energy density sufficient as a power supply for a portable electronic equipment, it is necessary to improve the stability of the cathode material in the range of electrode potential higher than 4 V versus Li/Li⁺ and in the temperature range of approximately -20 to +60 °C. Furthermore, in order to increase the capacity of the anode, coulombic efficiency of the carbon must be raised by improving its Li-doping/undoping capability.

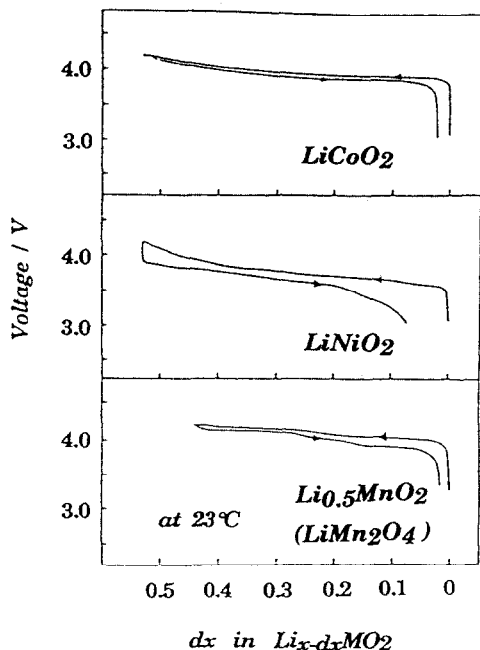


Fig. 1. Charge and discharge curves of $\text{Li}/\text{Li}_{1-dx}\text{MO}_2$ ($\text{M}=\text{Co}, \text{Ni}, \text{Mn}$); charge: maximum limit of 4.2 V, discharge: 3.3 V cutoff, and current density: $0.5 \text{ mA}/\text{cm}^2$.

Li_xMO_2 ($\text{M}=\text{Co}, \text{Ni}, \text{Mn}$) cathodes

For layered transition metal oxides LiCoO_2 , LiNiO_2 and spinel manganese oxide LiMn_2O_4 , electrode potentials become higher than 4 V versus Li/Li^+ by extracting Li from these compounds electrochemically in a nonaqueous electrolyte solution [4–7]. Figure 1 shows the low rate charge and discharge curves for rechargeable cells using the Li metal anode. As shown in Fig. 1, it is found that these cathode materials can be charged and discharged in the range of high voltage around 4 V. In the case of Li_xCoO_2 , the magnitude of the polarization is smaller and the capacity is larger compared with other transition metal oxides [2].

Lithium–carbon intercalation compound (Li–CIC) anode

Li–CIC can be obtained by electrochemically doping carbon with Li in nonaqueous electrolyte solutions. Therefore, by using Li containing cathodes such as those mentioned above, Li–CIC can be prepared inside the cell during the initial charge. This doping is desirable from the standpoint of battery production.

The quantity of Li in the carbon depends strongly on the species of carbon. As shown in Fig. 2, the charging capacity of non-graphitizable carbon such as polyfurfuryl alcohol derived carbon (PFA–C) [8–11] is larger than that of graphitizable carbon such as coke. It was also found that the capacity could be increased by the addition

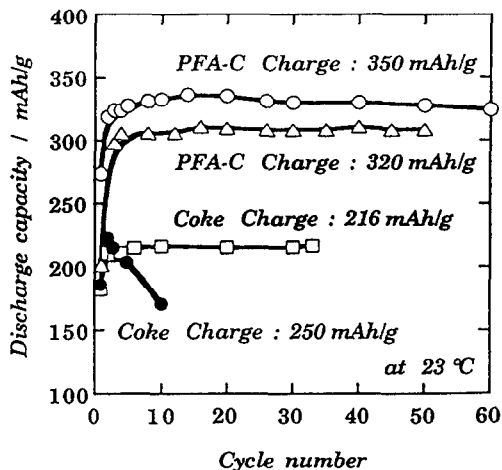


Fig. 2. Cycle performance of polyfurfuryl alcohol derived carbon (PFA-C) and acenaphthylene derived pitch coke; cathode: $\text{Li}_x\text{Ni}_y\text{Co}_{1-x-y}\text{O}_2$, electrolyte: PC-DME/1 M LiClO_4 .

of phosphorus-containing compounds such as phosphoric acid and phosphorus pentoxide before heat treatment.

Propylene carbonate(PC)-diethyl carbonate(DEC)/ LiPF_6 electrolyte solution

In these rechargeable cells, it is also required that the electrolyte remain stable even at potentials higher than 4 V versus Li/Li^+ and in the temperature range of approximately -20 to $+60$ °C.

As a result of investigating various nonaqueous electrolyte solutions, it is found that these requirements could be met by using PC-DEC solvent containing LiPF_6 . Figure 3 shows the retention of discharge capacity at 45 °C plotted against cycle number. As shown in Fig. 3, PC-DEC solvent exhibits a smaller decrease in the retention of discharge capacity than the PC-DME (1,2-dimethoxyethane) solvent [12].

Furthermore, as shown in Fig. 4, it is found that the same capacity is obtained in the temperature range of about 0 to 60 °C. At temperatures as low as -20 °C, approximately 80% of the maximum discharge capacity is available at low rate discharge (80 mA) and 50% at high rate (530 mA).

As for cycle life, in the case of the high rate discharge (530 mA), about 80% of the maximum discharge capacity is still obtained after 700 cycles at 25 °C.

Conclusion

By investigating various electrodes and electrolyte solutions, it was found that the lithium-ion rechargeable cell with LiCoO_2 and carbon electrodes such as polyfurfuryl alcohol derived carbon exhibits excellent performance by using propylene carbonate(PC)-diethyl carbonate(DEC)/ LiPF_6 in the temperature range of approximately -20 to $+60$ °C.

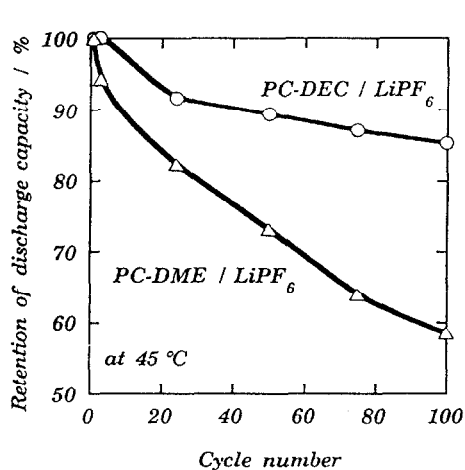


Fig. 3. Effect of electrolyte on cycle performance; charge: maximum limit 4.1 V, 1 A, 2.5 h, discharge: 2.7 V cutoff, 6 Ω , cell: cylindrical cell with wound electrodes and cell size: diameter 20 mm, height 50 mm.

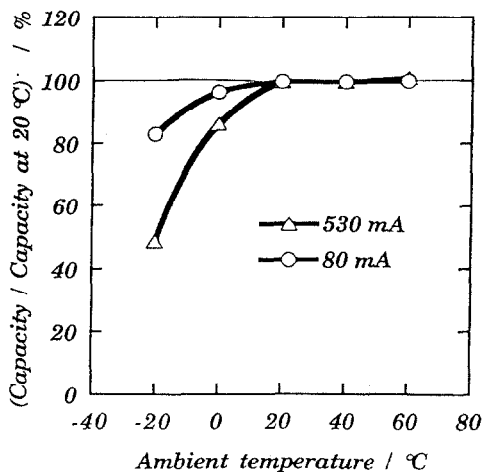


Fig. 4. Temperature characteristics of the discharge capacity; cell size: diameter 20 mm, height 50 mm.

References

- 1 K. M. Abraham, *J. Power Sources*, 7 (1981/1982) 43.
- 2 T. Nagaura, *JEC Battery Newsletter*, 2 (1991) 2-1.
- 3 M. Mohri, N. Yanagisawa, Y. Tajima, H. Tanaka, T. Mitaie, S. Nakajima, Y. Yoshimoto, T. Suzuki and H. Wada, *J. Power Sources*, 26 (1989) 545.
- 4 K. Mizushima, P. C. Jones, P. J. Wiseman and J. B. Goodenough, *Solid State Ionics* 3/4 (1981) 171.
- 5 A. Mendiboure, C. Delmas and P. Hagenmuller, *Mater. Res. Bull.*, 19 (1984) 1383.
- 6 J. B. Goodenough and K. Mizushima, *US Patent No. 4 302 518/20 87 858* (1981).
- 7 T. Ozuku, M. Kitagawa and T. Hirai, *J. Electrochem. Soc.*, 137 (1990) 769.
- 8 H. Imoto, H. Azuma, A. Omaru and Y. Nishi, *Ext. Abstr., 58th Meet. Electrochemical Society of Japan, Noda, Apr. 5-7, 1991*, p. 158.
- 9 A. Omaru, H. Azuma, H. Imoto and Y. Nishi, *Ext. Abstr., 58th Meet. Electrochemical Society of Japan, Noda, Apr. 5-7, 1991*, p. 158.
- 10 H. Azuma, A. Omaru and Y. Nishi, *Ext. Abstr., Fall Meet. Electrochemical Society of Japan, Nagoya, Oct. 12-13, 1991*, p. 132.
- 11 A. Omaru, H. Azuma, M. Aoki and Y. Nishi, *Ext. Abstr., Fall Meet. Electrochemical Society of Japan, Nagoya, Oct. 12-13, 1991*, p. 132.
- 12 S. Mashiko, M. Yokogawa and T. Nagaura, *Ext. Abstr., 32nd Battery Symp. Japan, Kyoto, Sept. 17-19, 1991*, p. 33.