Influences of the electrolyte composition on the charge and discharge characteristics of $LiCr_{0.1}Mn_{1.9}O_4$ positive electrode

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Abstract

The charge and discharge characteristics of chromium-substituted lithium manganate spinel, $LiCr_{0.1}Mn_{1.9}O_4$, have been studied in organic electrolyte solutions with different compositions. The rate capability and the cycle performance of the oxide cathode depended much on the electrolyte composition. Higher initial capacity was observed in the electrolyte solution showing higher ionic conductivity. Good cycle performance was obtained in $LiBF_4$ solutions with ternary solvent systems containing 1,2-dimethoxyethane (DME). Addition of Li_2CO_3 to the $LiPF_6$ solution improved the cycleability of the oxide cathode. The electrolyte composition giving lower impedance at the oxide/solution interface showed less capacity degradation during the charge/discharge cycles. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The charge and discharge performances of insertion-type electrodes for lithium- (Li) ion batteries are varied with the composition of the organic electrolyte solution [1,2]. It is important to establish an optimum composition of the electrolyte system for a specific combination of the positive and negative electrodes. Up to the present, however, little has been known about the details in the effects of the electrolyte composition on the electrode characteristics in Li-ion battery systems. We have investigated the influences of the electrolyte composition on the cycling performances of $LiNiO_2$ [3,4] and $LiMn_2O_4$ [5–7] cathodes. The electrolyte composition significantly affected the rate capability and cycle durability of the oxide cathodes. Especially, the cycle performance of $LiMn_2O_4$ depended much on the sort of the electrolytic salt [7].

In this work, we have examined the electrode characteristics of chromium-substituted lithium manganate spinel, $LiCr_{0.1}Mn_{1.9}O_4$ [8–10], in organic electrolyte solutions with different salt/solvent combinations. The cathode (positive electrode) performances are discussed in relation with the ac impedance behavior at the electrode/electrolyte interphase.

2. Experimental

Ethylene carbonate (EC) or propylene carbonate (PC) was mixed with a low viscosity solvent (LVS), dimethyl carbonate (DMC), with and without 1,2-dimethoxyethane (DME). The mixing ratio of EC (or PC) and LVS was kept constant to 50/50 by volume. The electrolytic salts were $LiClO_4$, $LiPF_6$ and $LiBF_4$ (1 mol dm^{-3}). The test electrode was composed of 90 wt.% of active material, $LiCr_{0.1}Mn_{1.9}O_4$ (Tosoh), mixed with 5 wt.% of acetylene black as a conducting support and 5 wt.% of a fluoro-resin binder. The charge and discharge characteristics were measured under constant-current conditions using a 2032 coin-type (two-electrode) cell with a Li metal counter electrode. The interfacial behavior was investigated by an ac impedance method using a three electrode system. The measurements were carried out for the electrodes after fully-charged (deintercalation of Li) and then half-discharged (intercalation of Li) under open circuit conditions (ac amplitude: 10 $mV_{p–p}$, 65 kHz–10 mHz) [7]. All experiments were carried out under a dry-Ar atmosphere at room temperature (18–25°C).

3. Results and discussion

Fig. 1 shows the variations in the discharge capacity of $LiCr_{0.1}Mn_{1.9}O_4$ with the cycle number, measured in

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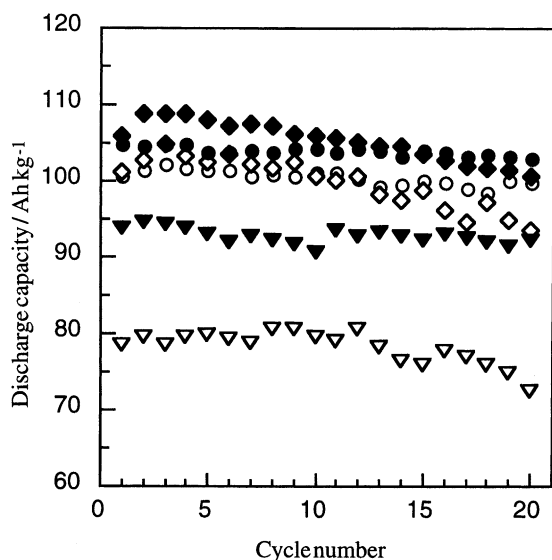*E-mail address*: morita@po.cc.yamaguchi-u.ac.jp (M. Morita).

Fig. 1. Variations in the discharge capacity of $LiCr_{0.1}Mn_{1.9}O_4$ with cycle number in 1 mol dm^{-3} LiX/([EC or PC] + DMC) (50 + 50 by volume). Current density: 1.0 mA cm^{-2}, cut-off voltage: 3.4–4.4 V, X = ClO$_4$ (○, ●), PF$_6$ (◇, ◆), BF$_4$ (▽, ▼), open symbols: PC + DMC, closed symbols: EC + DMC.

Fig. 2. Variations in the discharge capacity of $LiCr_{0.1}Mn_{1.9}O_4$ with cycle number in 1 mol dm^{-3} LiX/(EC + LVS) (50 + 50 by volume). Current density: 1.0 mA cm^{-2}, cut-off voltage: 3.4–4.4 V, (●): LiBF$_4$/(EC+ DMC) (50+50), (◇): LiBF$_4$/(EC + DMC + DME) (50 + 25 + 25), (○): LiBF$_4$/(EC + DMC + DME) (50 + 17 + 33), (+): LiPF$_6$/(EC + DMC) (50 + 50).

PC + DMC and EC + DMC (50 + 50 vol.%) mixed solvents dissolving different Li salts. The discharge capacity and its cycle variation depended on the electrolyte composition. With respect to the solvent, the discharge capacity measured in PC + DMC was lower than that in the EC-based solution. Also the capacity at the initial cycle decreased in the order of LiPF$_6$ > LiClO$_4$ > LiBF$_4$, which was generally consistent with the order of the ionic conductivity of the solution using mixed EC (or PC) and DMC solvents. The rate capability of the cathode for discharging also depended on the electrolyte solution [7]. The discharge capacity in LiPF$_6$ was high at initial few cycles, but it gradually decreased with cycle repeating.

The discharge capacity in the LiBF$_4$ solution with EC + DMC (50 + 50 by volume) solvent was rather low even at low discharge rates. However, the capacity loss with the cycle repeating was quite low in the solutions containing LiBF$_4$. As the LiBF$_4$ salt is superior to other salts from the viewpoints of safety and environmental compatibility, we have tried to improve the discharge performances of $LiCr_{0.1}Mn_{1.9}O_4$ in the solutions using LiBF$_4$ as the salt. Partial substitution of DMC with equal volume of DME was efficient for the improvements in the ionic conductivity of the solution. Fig. 2 shows the effect of the DME substitution in LiBF$_4$/(EC + DMC) on the discharge capacity. The solution based on the ternary solvent system, LiBF$_4$/(EC + DMC + DME), gave higher discharge capacity than the solution based on the binary solvent system, LiBF$_4$/(EC + DMC). The current density shown in Fig. 2 (1.0 mA cm^{-2}) corresponded to the rate condition of about 0.5 C. Almost ideal (theoretical) discharge capacity of ca. 115 Ah kg^{-1} was obtained for $LiCr_{0.1}Mn_{1.9}O_4$ in

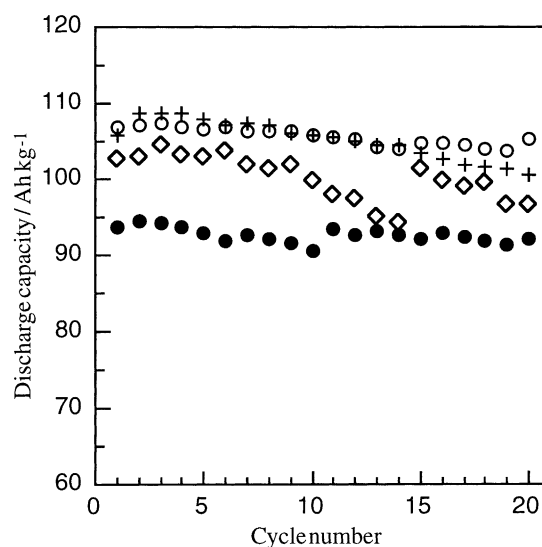LiBF$_4$/(EC + DMC + DME) system under the rate condition of 0.5 mA cm^{-2} (0.25 C). The ternary solvent electrolyte also lead to better rate capability than the binary solvent EC + DMC system. That is, about 80% of the theoretical discharge capacity was attained even under 1 C condition. The DME component improves the transport property at the electrode/electrolyte interface, due to its low viscosity and good affinity to Li$^+$ in the solution. The discharge capacity did not decreased with the repeated charge/discharge cycles in this electrolyte system.

Degradation in the discharge capacity with cycle repeating in LiPF$_6$ solution was also suppressed by addition of Li$_2$CO$_3$ to the electrolyte solution. Fig. 3 presents a typical result of the effect of the Li$_2$CO$_3$ addition. In the LiPF$_6$ solution saturated with Li$_2$CO$_3$, the capacity loss after repeated cycles is low compared with that in the solution without Li$_2$CO$_3$. The organic solutions of LiPF$_6$ usually contain small amounts of HF that is evolved by the reaction of LiPF$_6$ and the contaminant water in the system. Dissolution of the spinel oxide, which is accelerated by the HF component in the electrolyte, is one of the causes for degradation of the cycling performances [11,12]. The addition of Li$_2$CO$_3$ would minimize the evolution of free HF in the electrolyte system.

The ac impedance measurements were carried out for the $LiCr_{0.1}Mn_{1.9}O_4$ cathode in organic electrolytes with different compositions. Fig. 4 shows Cole–Cole plots of the impedance measured under OCV conditions after charging (anodic de-intercalation of Li) and discharging (cathodic intercalation of Li) to about 50% of depth of discharge (DOD). We can regard that each plot consists of three parts; an arc in the high frequency region, a small semicircle in the
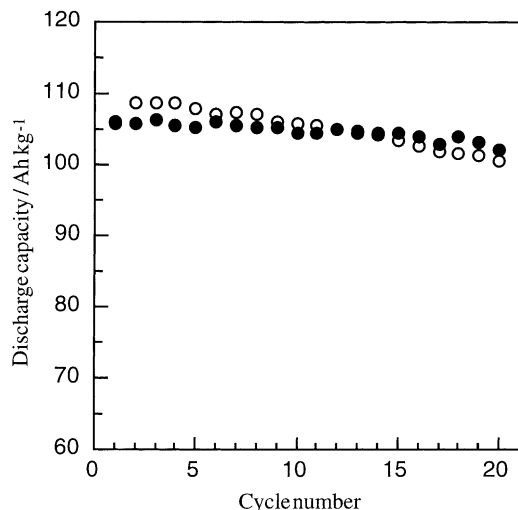
Fig. 3. Variations in the discharge capacity of $LiCr_{0.1}Mn_{1.9}O_4$ with cycle number in 1 mol dm^{-3} $LiPF_6/(EC + DMC)$ (50 + 50) (○) and in the same solution saturated with Li_2CO_3 (●).
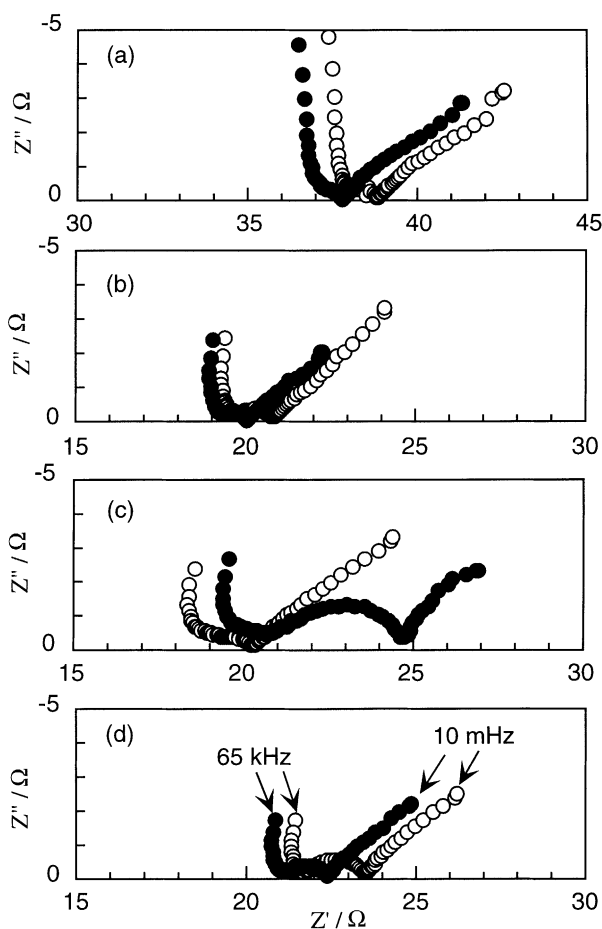

Fig. 4. Cole–Cole plots of the ac impedance for $Li_xCr_{0.1}Mn_{1.9}O_4$ in (a) $LiBF_4/(EC + DMC)$, (b) $LiBF_4/(EC + DMC + DME)$, (c) $LiPF_6/(EC+ DMC)$ and (d) $LiPF_6/(EC + DMC)$ saturated with Li_2CO_3. (○): After fully-charged ($x = 0.22$–0.28), (●): after half-discharged ($x = 0.54$–0.58).

middle frequency region and a straight line with a slope of 45° in the low frequency region [5,7]. The shape of the arc in the high frequency region (65–5 kHz) depended on the cell configuration, which suggests that the impedance may include a pseudo capacitance based on such an incidental component as the contact with the current collector. However, the intersection point on the Z'-axis did not change with the cell configuration. Thus, it corresponds to a bulk impedance component based on a total dc resistance of the electrolyte and the electrode itself. The straight line with a slope of 45° in the lower frequency region reveals that the electrode system is controlled by a mass transport (diffusion) process [5,7,13]. The most striking difference in the impedance spectra among the electrolyte systems is the semicircle observed in the middle frequency region, which may be called an interface impedance. The physical meaning of the interface impedance is not clear at this stage, but it has formally been assigned to a parallel combination of a capacitance and a resistance of the surface film formed on the oxide [7,13]. In the solutions containing $LiClO_4$ and $LiBF_4$, the size of the semicircle was rather small (Fig. 4(a) and (b)), whereas the solutions containing $LiPF_6$ gave larger sizes of the semicircles, especially for the electrode after the discharge (Fig. 4(c), closed symbols). The addition of Li_2CO_3 to the solution of $LiPF_6$ lead to the reduction of the interface resistance, as shown in Fig. 4(d). This is somewhat similar to the case of CO_2 saturation in alkyl carbonate-based electrolytes that improves the cycling performances and the interfacial chemistry of Li metal anodes [14–17].

Relationships between the charge/discharge performances and the impedance characteristics of the $LiCr_{0.1}Mn_{1.9}O_4$ electrode were examined in the electrolytic solutions with different compositions. The results are summarized in Fig. 5, where the initial discharge capacity (Q, Ah kg^{-1} at the 2nd cycle) and the capacity loss during the first 10 cycles (ΔQ, Ah kg^{-1}) are plotted against the bulk impedance, R_{bulk}, and the interfacial impedance, R_{int}, respectively. Higher initial capacity was obtained in the solutions giving lower R_{bulk}, suggesting that the conductance of the electrolytic solution almost determines the rate capability of the cathode at the initial cycles. The R_{int} value in Fig. 5(B) is that observed for the electrode after the first charge followed by the subsequent discharge (ca. 50% DOD). It tends that the solutions giving higher R_{int} values lead to higher capacity loss during the repeated cycles. This strongly suggests that some interfacial process on the oxide cathode causes the capacity loss during the repeated cycle. One of the possible processes is the surface reaction that form a less-conductive film on the oxide [13]. Interestingly, the interfacial property at the initial stage almost determines the subsequent cycling performance of the spinel oxide. Moreover, it must be noted that the high interfacial impedance observed for the electrode discharged in $LiPF_6$ solutions, as shown in Fig. 4(c), was decreased again when the electrode recharged up to $x = 0.2$ in $Li_xCr_{0.1}Mn_{1.9}O_2$.
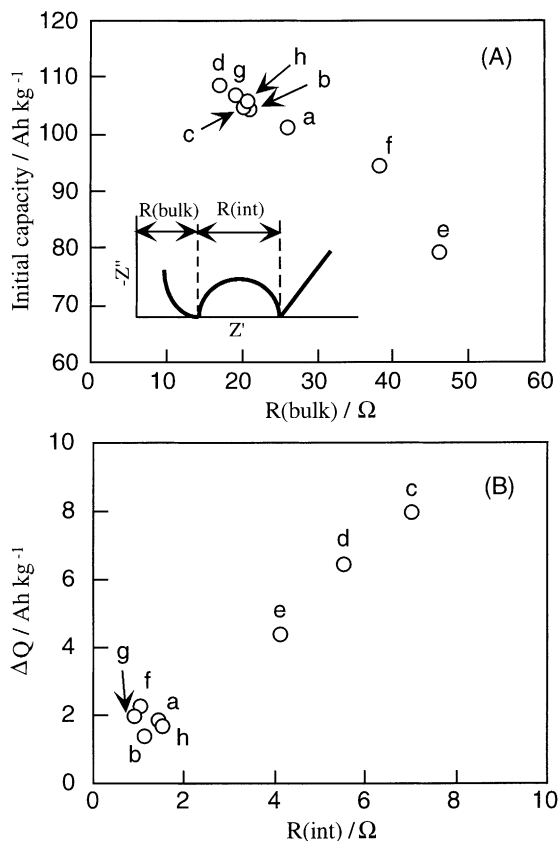
Fig. 5. Relationships between (A) initial discharge capacity and bulk impedance (R_{bulk}), and (B) between capacity loss and interfacial impedance (R_{int}) for $LiCr_{0.1}Mn_{1.9}O_4$. (a): $LiClO_4/PC + DMC$, (b): $LiClO_4/EC + DMC$, (c): $LiPF_6/PC + DMC$, (d): $LiPF_6/EC + DMC$, (e): $LiBF_4/PC + DMC$, (f): $LiBF_4/EC + DMC$, (g): $LiBF_4/EC + DMC+ DME$, (h): $LiPF_6/EC + DMC$ with Li_2CO_3.

Although, the details of the interfacial chemistry are not clear for this electrode/electrolyte system, it is definite that good cycle performances of the $LiCr_{0.1}Mn_{1.9}O_4$ cathode will be extracted for the electrolytes giving low interfacial impedance.

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