Structural change during charge—discharge for iron substituted lithium manganese oxide

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HIGHLIGHTS

- Fe-substituted Li_2MnO_3 was prepared by coprecipitation—calcination method.
- On initial charging, Fe ion moved to the tetrahedral $8j$ site.
- Stability of layered rock-salt structure sensitive to the mode of initial charging.

ARTICLE INFO

ABSTRACT

For this study, Fe-substituted Li_2MnO_3 ($Li_{1+x}(Fe_{0.25}Mn_{0.75})_{1-x}O_2$, $0 < x < 1/3$) was prepared using coprecipitation—calcination. The change in the cation distribution was examined after charge—discharge using a monoclinic Li_2MnO_3 unit cell ($C2/m$). At the initial Li-extraction, Fe ion moved to the tetrahedral $8j$ site. At the end of charging, transition metals moved from $4g$ and $2b$ sites in (Mn, Fe)—Li layer to $2c$ and $4h$ sites in the Li-layer via $4i$ and $8j$ sites. The cation random distribution was maintained after the end of discharging. The stability of layered rock-salt phase after cycle testing depended on the mode of charging; although the positive electrode decomposed to a mixture of layered rock-salt and spinel phases by typical galvanostatic charging, the positive electrode remained a single phase with a layered rock-salt structure by application of stepwise charging. Careful control of the charging mode at the initial cycle is important for Fe-substituted Li_2MnO_3 positive electrode material.

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1. Introduction

Large-scale lithium-ion batteries are now a necessary power source for use in electrical vehicles. The constituent positive electrode material for the battery must have high capacity. Among the proposed positive electrode materials, Li-rich layered oxide, $LiMO_2$-Li_2MnO_3 (M = $Ni_{1/2}Mn_{1/2}$, $Ni_{1/3}Mn_{1/3}Co_{1/3}$) solid solution [1,2] is attractive because of its specific capacity higher than about 200 mAh·g^{-1}. Although the charge—discharge mechanism remains unclear, participation of oxide ion as a redox center as well as Co and Ni ions has been suspected [3–6]. Structural change during the charge—discharge cycle has also examined [5,7—9]. Lu and Dahn proposed oxygen loss from the structure after first charging to 4.8 V [7]. Jiang et al. observed stabilization of the cation random structure at discharged state after high-voltage charging at voltages higher than 4.6 V [9].

$LiFeO_2$—Li_2MnO_3 solid solution (Fe substituted Li_2MnO_3, $Li_{1+x}(Fe_yMn_{1-y})_{1-x}O_2$, $0 < x < 1/3$, $0 < y \leq 0.5$) is also attractive as a high-capacity 3 V class positive electrode material (>200 mAh·g^{-1}) [10—12] because of its utilization of cheap and naturally abundant Fe. The complex charge—discharge mechanism was examined mainly using analytical TEM [13—15]. The sample with $y = 0.5$ was a composite consisting of layered Fe-substituted Li_2MnO_3 and cubic Mn-substituted $LiFeO_2$ [13]. On initial charging, Li extraction occurred from the cubic phase below 4.5 V. Then Li_2O extraction occurred from the layered phase above 4.5 V [14]. Oxide ion

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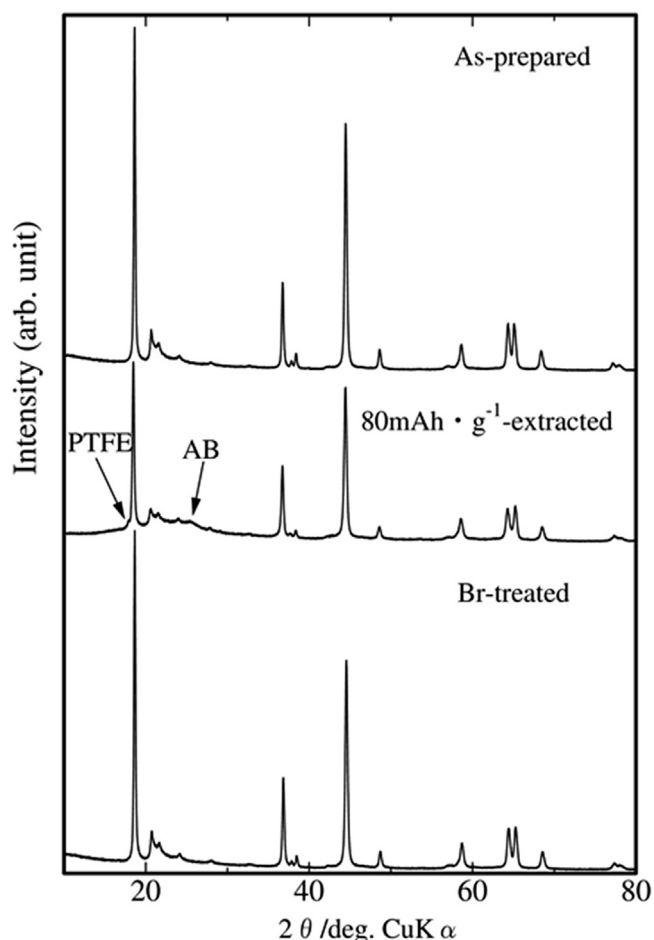 E-mail address: m-tabuchi@aist.go.jp (M. Tabuchi).

Fig. 1. X-ray diffraction patterns for as-prepared, 80 mAh·g^{-1}-extracted, and Br-treated samples.

extraction and insertion was observed at the end of initial charging and discharging, respectively, suggesting that oxide ions act as a redox center not only during charging but also during discharging [15]. Stabilization of cation random structure was observed at 1 cycled sample [15] like in Ni substituted Li$_2$MnO$_3$ [9]. The electrochemical characteristics of sample with $y = 0.3$ were improved drastically using stepwise charging [16], as reported by Ito et al. [17]. Application of stepwise charging engenders suppression of the initial O$_2$ gas generation on charging up to 4.8 V and improves cyclability of C/Li$_{1+x}$(Fe$_{0.3}$Mn$_{0.7}$)$_{1-x}$O$_2$ cell [17]. However, the effects of the stepwise charging on structural change and the cyclability remain unknown.

As described in this paper, the structural change of the sample with $y = 0.25$ was examined after stepwise application and galvanostatic charging up to the tenth cycle. *Ex-situ* X-ray Rietveld analysis was used mainly by combination with Fe and Mn K-edge X-ray absorption fine structure (XAFS), magnetization measurement, neutron diffraction, and ^{57}Fe Mössbauer spectroscopy.

2. Experimental

Li$_{1+x}$(Fe$_{0.25}$Mn$_{0.75}$)$_{1-x}$O$_2$ has been prepared by coprecipitation–calcination method (0.25 mol/batch, as-prepared sample). For the coprecipitation process, a Fe–Mn mixed aqueous solution was prepared by dissolving Fe(NO$_3$)$_3$·9H$_2$O and MnCl$_2$·4H$_2$O (reagent grade; Wako Pure Chemical Industries Ltd.) into distilled water. The Fe–Mn solution was dripped into cooled LiOH solution including ethanol (antifreeze reagent) at −10 °C for 2–3 h to avoid the formation of spinel ferrite phases. The Fe–Mn coprecipitate was aged by bubbling air for 2 days. It was then isolated by filtration. The aged coprecipitate was mixed with LiOH aqueous solution including 0.375 mol of LiOH·H$_2$O. Then the mixture was dried at 100 °C. During the calcination process, the dried mixture was calcined at 850 °C for 1 h in air atmosphere after pulverization. The product was washed using distilled water, filtered, and then dried at 100 °C.

Table 1
Structural parameters resulted from X-ray Rietveld analysis using monoclinic layered rock-salt Li$_2$MnO$_3$ ($C2/m$) and cubic spinel ($Fd\overline{3}m$) unit cells and spontaneous magnetization values obtained from magnetization measurement.

(a) Fraction and lattice parameters of both phases and spontaneous magnetization values

Sample	Layered rock-salt phase ($C2/m$)						Spinel phase($Fd\overline{3}m$)		Spontaneous magnetization/Gcm^3·g^{-1}
	Fraction/%	a/Å	b/Å	c/Å	β/deg.	V/Å^3	Fraction/%	a/Å	
As-prepared	100	4.9673(6)	8.5809(7)	5.0304(4)	109.177(10)	202.5(7)	–	–	0.0054(10)
Br-treated	100	4.9513(7)	8.5638(8)	5.0269(5)	109.135(14)	201.4(9)	–	–	0.0005(7)
80 mAh/g extracted	100	4.9416(7)	8.5512(10)	5.0269(5)	109.212(11)	200.6(8)	–	–	0.008(3)
5c-S	100	4.9832(10)	8.6114(15)	4.9997(8)	109.628(16)	202.1(12)	–	–	0.008(2)
5d-S	100	5.0145(10)	8.6824(11)	5.0674(7)	109.303(18)	208.2(13)	–	–	0.008(2)
14d-S	100	5.0368(7)	8.6644(9)	5.0731(6)	109.405(10)	208.8(7)	–	–	0.0072(11)
1c-G	100	4.9680(11)	8.5914(16)	4.9717(8)	109.553(19)	200.0(12)	–	–	0.008(2)
1d-G	100	5.0795(10)	8.7965(13)	5.1046(7)	109.423(16)	215.1(12)	–	–	0.007(2)
10d-G	85.39	5.0346(11)	8.8560(14)	5.0920(9)	109.113(13)	214.5(10)	14.61	8.532(5)	0.01239(8)

(b) Transition metal occupancy at each site (g) and sum of occupancies (g_{total}) for Each phase

Sample	Layered rock-salt phase ($C2/m$)							Spinel phase($Fd\overline{3}m$)		
	g_{4g}	g_{2b}	g_{2c}	g_{4h}	g_{4i}	g_{8j}	g_{total}[a]	g_{8a}	g_{16d}	g_{total}[b]
As-prepared	0.742(4)	0.451(3)	0(fixed)	0.0838(19)	0(fixed)	0(fixed)	0.701(5)	–	–	–
Br-treated	0.739(4)	0.409(4)	0(fixed)	0.011(2)	0(fixed)	0.0248(9)	0.668(7)	–	–	–
80 mAh/g extracted	0.606(4)	0.403(4)	0.0735(3)	0.067(2)	0(fixed)	0.0681(9)	0.698(7)	–	–	–
5c-S	0.566(7)	0.564(10)	0.119(5)	0.119(3)	0.065(4)	0.071(2)	0.822(14)	–	–	–
5d-S	0.567(4)	0.522(6)	0.142(3)	0.047(2)	0.047(2)	0.0357(15)	0.743(11)	–	–	–
14d-S	0.580(4)	0.647(5)	0 (fixed)	0.1684(17)	0 (fixed)	0.0682(7)	0.805(16)	–	–	–
1c-G	0.511(6)	0.577(9)	0.176(5)	0.124(3)	0.081(3)	0.0811(19)	0.837(12)	–	–	–
1d-G	0.501(4)	0.529(7)	0.215(4)	0.162(2)	0.033(3)	0.0334(16)	0.756(10)	–	–	–
10d-G	0.498(5)	0.522(9)	0.238(7)	0.048(5)	0.104(5)	0.092(3)	0.809(14)	0.97(2)	1(fixed)	2.97(2)

[a] g_{total} means transition metal content per chemical formula, as calculated from the equation $g_{total}=(2g_{4g} + g_{2g})/3+(g_{2c} + 2g_{4h})/3 + 2(g_{4i} + 2g_{8j})/3$.
[b] g_{total} means transition metal content per chemical formula, as calculated from the equation $g_{total} = g_{8a} + 2g_{16d}$.