Rietveld Refinement of Oxysulfide $LiAl_{0.24}Mn_{1.76}O_{4-y}S_y$ (y = 0, 0.02) Spinel Materials

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Abstract

$LiAl_{0.24}Mn_{1.76}O_{4-y}S_y$ (y = 0, 0.02) were synthesized by the sol-gel method. Both structures were refined by Rietveld method, its structure refined as a cubic spinel, space group Fd-3m, a = 8.17937(30) Å and 8.18331(19) Å respectively. Though it has been made a charge/discharge experiment above 20 times, there was no change of 3 V/4 V capacity degradation. It was considered that the volume change of MnO_6 octahedron induced by sulfur substitution plays a key role in keeping the 3 V/4 V capacity. The refined composition of the compound could be confirmed with the ICP analysis.

1. Introduction

Spinel $LiMn_2O_4$ have generated great interest as the most promising cathode materials (positive electrodes) for lithium secondary batteries, due to its high energy density, low cost, abundance, and non-toxicity. $Li_xMn_2O_4$ (x = 1) has a cubic spinel structure with space group symmetry Fd-3m, in which the Li^+ and $Mn^{3+/4+}$ ions are located on the 8a tetrahedral sites and the 16d octahedral sites of the structure, respectively.[1,2]

Lithium extraction from the 8a tetrahedral sites in $Li_xMn_2O_4$ (i.e., for 0≤x≤1) occurs at 4 V vs. metallic lithium. In the 4 V region, it appears that the cubic structure of the material is maintained during the extraction and insertion of Li^+ ions, but the capacity of the spinel electrode slowly losses during cycling. For 1≤x≤2, it has been reported that Li^+ ions are inserted into the empty 16c octahedral sites of the spinel structure at approximately 3 V. The lithium insertion into $Li_xMn_2O_4$ results in the transition of the structure from cubic into tetragonal $Li_2Mn_2O_4$, which is accompanied by the Jahn-Teller distortion due to the reduction of the average oxidation state of Mn from 3.5 to 3.0. The increased concentration of Mn^{3+} ions in the host structure

reduces the crystal symmetry from cubic (c/a = 1) to tetragonal symmetry (c/a = 1.16), which give rise to rapid capacity fading.[3,4] Thus the spinel $Li_xMn_2O_4$ is more stable on high voltage region and is limited to use only for the 4 V region.

Many attempts to overcome the Jahn-Teller distortion have been done by synthesizing lithium rich spinels or aluminium ion-doped spinels.[5,6] Lee and Yoshio[7] suggested that the reason why Al-doped spinel has performance degradation in 3 V region. Lately Sun et al.[8] showed that by substitution for sulfur, the capacity fading decreases in the 3 V region.

In this work, we synthesized spinel materials, oxysulfide $LiAl_{0.24}Mn_{1.76}O_{4-y}S_y$ (y = 0, 0.02) using the sol-gel method and evaluate their crystal structures by Rietveld refinement and electrochemical performance.

2. Experimentals

$LiAl_{0.24}Mn_{1.76}O_{4-y}S_y$ (y = 0, 0.02) powders were prepared by the sol-gel method as reported in our previous work.[8] $Li_{1.05}Al_{0.25}Mn_{1.75}O_{3.85}S_{0.15}$ was a starting composition of $LiAl_{0.24}Mn_{1.76}O_{3.98}S_{0.02}$. $Li(CH_3COO) \cdot H_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$, Li_2S, and $Al(NO_3)_3 \cdot 9H_2O$

(cationic ratio of Li : Mn : Li : Al = 0.75 : 1.75 : 0.3 : 0.25) were dissolved in the distilled water, and added dropwise to a continuously stirred aqueous solution of glycolic acid. The pH of the solution was adjusted 8.5~9.5 and the resultant solution was evaporated at 70~80°C until a transparent sol and gel was obtained. The resulting gel precursors were decomposed at 500°C for 10 h in air. The decomposed powders were calcined at 800°C in air for 10 h and then in flowing oxygen for 15 h.

The X-ray diffraction data were collected by using X-ray diffractometer (Model Geigerflex, D/max-B, Rigaku Co., Tokyo, Japan; Cu $K\alpha$ radiation, produced at 40 kV and 35 mA) equipped with a diffracted beam graphite monochromator. The scan width and time was 0.02° and 10 sec at the range of 15 to 140° 2θ. The measured data were refined by the FULLPROF (Rodriguez-Carvajal,[9] 1993). The chemical composition was determined by chemical analysis using an inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Charge-discharge cycles were performed in CR2032 coin type cells. The cell consisted of a cathode and a lithium metal anode separated by a porous polypropylene film. For the fabrication of the electrode, the mixture, which contained 25 mg LiAl₀.₂₄Mn₁.₇₆O₃.₉₈S₀.₀₂ powders and 15 mg conducting binder (10 mg TAB and 5 mg graphite), was pressed on 2.0 cm² stainless screen at 800 kg/cm². The used electrolyte was a 1 : 2 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) containing 1 M LiPF₆ by volume. The charge-discharge cycle was performed galvanostatically in the 3 V and 4 V region at a current rate of C/3 (0.4 mA/cm²).

3. Results and Discussion

3-1. Structure refinement of LiAl₀.₂₄Mn₁.₇₆O₄₋ᵧSᵧ (y = 0, 0.02) by rietveld refinement

Figure 1 shows typical XRD patterns of LiMn₁.₇₆Al₀.₂₄O₄₋ᵧSᵧ which can be indexed with the spinel structure (space group Fd-3m). To clarify where Al and S are placed, Rietveld refinement was carried out. Figure 2 shows the x-ray diffraction patterns which represents the observed, calculated and the difference profiles in LiAl₀.₂₄Mn₁.₇₆O₄.₀₀ and LiAl₀.₂₄Mn₁.₇₆O₃.₉₈S₀.₀₂
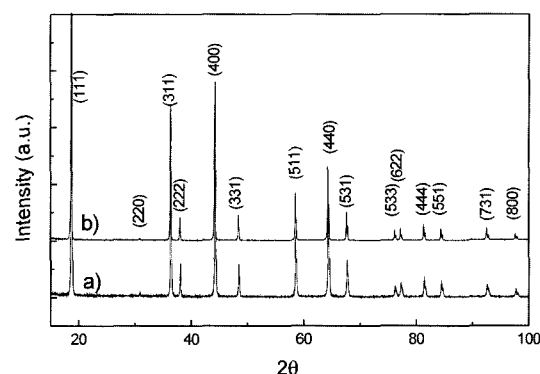
Fig. 1. Typical X-ray powder pattern of LiAl₀.₂₄Mn₁.₇₆O₄ and LiAl₀.₂₄Mn₁.₇₆O₃.₉₈S₀.₀₂.
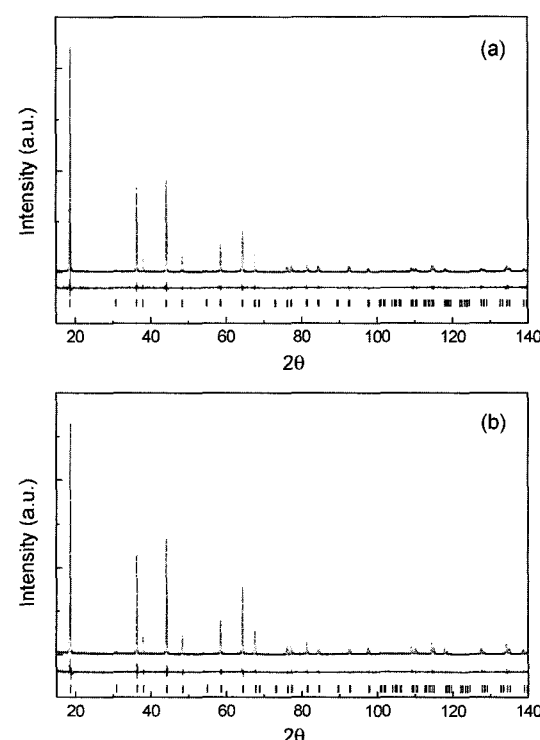
Fig. 2. Observed, calculated and difference profiles for LiAl₀.₂₄Mn₁.₇₆O₄₋ᵧSᵧ; a) y = 0.0, b) y = 0.02.

respectively. The structure of LiMn₂₋ₓAlₓO₄₋ᵧSᵧ was refined with the space group Fd-3m, which defines an aristotype cubic spinel. For better refinement results, we constrained the s.o.fs of Mn/Al, and O/S to be 0.5 and 1 respectively. In this space group with spinel structure, the tetrahedral Li resides on the 8a sites, the octahedral Al and Mn are randomly

Table 1. Refined structural parameters of LiAl$_{0.24}$Mn$_{1.76}$O$_{4.00}$ and LiAl$_{0.24}$Mn$_{1.76}$O$_{3.98}$S$_{0.02}$

i) LiAl$_{0.24}$Mn$_{1.76}$O$_{4.00}$: Space group: Fd-3m; a = 8.17937(30) Å
R$_p$ = 8.38%, R$_{wp}$ = 13.8%. χ^2 (Goodness of fit) = 1.74

Atom	Site	x	y	z	B	Occupancy Refined	Occupancy ICP's
Li	8a	0.1250	0.1250	0.1250	1.22(33)	0.249(9)	0.265
Mn	16d	0.5000	0.5000	0.5000	0.58(2)	0.428(2)	0.440
Al	16d	0.5000	0.5000	0.5000	0.58(2)	0.072(2)	0.060
O	32e	0.2628(2)	0.2628(2)	0.2628(2)	1.42(8)	1.000(0)	0.995

ii) LiAl$_{0.24}$Mn$_{1.76}$O$_{3.98}$S$_{0.02}$: Space group: Fd-3m; a = 8.18331(19) Å
R$_p$ = 9.03%, R$_{wp}$ = 13.5%. χ^2 (Goodness of fit) = 1.26

Atom	Site	x	y	Z	B	Occupancy Refined	Occupancy ICP's
Li	8a	0.1250	0.1250	0.1250	1.34(10)	0.272(10)	0.265
Mn	16d	0.5000	0.5000	0.5000	0.48(3)	0.449(2)	0.440
Al	16d	0.5000	0.5000	0.5000	0.48(3)	0.051(2)	0.060
O	32e	0.2644(2)	0.2644(2)	0.2644(2)	1.63(9)	0.992(3)	0.995
S	32e	0.2644(2)	0.2644(2)	0.2644(2)	1.63(9)	0.008(3)	0.005

$$R_p = \frac{\sum |y_i(obs) - y_i(calc)|}{\sum y_i(obs)} \quad R_{wp} = \left\{ \frac{\sum w_i(y_i(obs) - y_i(calc))^2}{\sum w_i(y_i(obs))^2} \right\}^{1/2} \quad R_e = \left\{ \frac{(N - P + C)}{\sum w_i y_i(obs)} \right\}^{1/2}$$

χ^2 (Goodness of fit) = $(R_{wp}/R_e)^2$

$y_i(obs)$ and $y_i(calc)$ are the observed and calculated intensities at the ith step respectively, $I_k(obs)$ and $I_k(calc)$ are the observed and calculated intensities assigned to the Kth Bragg reflection. N is total number of points, and P and C are the number of refined and constraint parameter. w_i is the weight factor.

distributed on 16d sites, and the O and S on the 32e sites. The obtained parameters in the refinements for LiMn$_{2-x}$Al$_x$O$_{4-y}$S$_y$ are summarized in Table 1. The refined composition of LiAl$_{0.24}$Mn$_{1.76}$O$_{3.98}$S$_{0.02}$ are in good agreement with the stoichiometric one determined by ICP analysis. Refinement calculated in using the model which the excess Li ion exists in

the 16c site, lead to negative site occupancy. So we concluded that the Li ion exists in 16d site like as the normal spinel. The isotropic temperature factors of Al and S were refined with the condition which are the same as the Mn and O respectively. As the sulfur (r_S^{-2} = 0.180 Å) is substituted for oxygen (r_O^{-2} = 0.140 Å), the bond length of Mn(Al)-O decreases

Table 2. Bond lengths and angles of MnO$_6$ octahedra refined in spinel LiAl$_{0.24}$Mn$_{1.76}$O$_{4.00}$ and LiAl$_{0.24}$Mn$_{1.76}$O$_{3.98}$S$_{0.02}$

	LiAl$_{0.24}$Mn$_{1.76}$O$_{4.00}$	LiAl$_{0.24}$Mn$_{1.76}$O$_{3.98}$S$_{0.02}$	LiMn$_2$O$_4$
Bond length [Å]	1.9454 [×6]	1.9349 [×6]	1.937 [×4] 2.286 [×2]
Oxygen position parameter [x]	0.26285	0.26444	0.265
Angles [degree]			
O1-Mn(Al)-O2	83.64	82.80	86
O1-Mn(Al)-O3	83.64	82.80	88
O1-Mn(Al)-O4	96.35	97.20	92
O1-Mn(Al)-O5	96.35	97.20	94
O1-Mn(Al)-O6	180.0	180.0	180
Volume of MnO$_6$ [Å^3]	9.727	9.551	

and then the cell parameter decreases. In the result of sulfur substitution the volume of MnO_6 polyhedron changes from 9.727 $Å^3$ to 9.551 $Å^3$, a reduction of 1.84%. It is considered that this volume change makes the mobility of Li ion in $LiAl_{0.24}Mn_{1.76}O_{3.98}S_{0.02}$ increase and influences the capacity fading in the 3 V, which will be explained in next section.

3-2. Characterization by charge/discharge analysis

The chemical analysis data showed the sample to be $LiAl_{0.24}Mn_{1.76}O_{3.98}S_{0.02}$ and the average oxidation state of manganese in the powders was 3.55. Figure 3 shows scanning electron micrograph (SEM) images of the as-prepared $LiAl_{0.24}Mn_{1.76}O_{3.98}S_{0.02}$ powders. The particle morphology of oxysulfide spinel powders is analogous to that of single-crystal-like gold with a cubic structure, which is quite different from that of stoichiometric spinel $LiMn_2O_4$. The particles are shaped into well-developed polyhedra, mainly octahedral configuration bounded by eight (111) planes. The average diameter of the particles is 1 μm.

Figure 4(a) shows the charge-discharge curves of the oxysulfide spinel electrode measured in the voltage range of 4.4~3.0 V. The measured curves have only one plateau due to a large amount of Al substitution for Mn. Although the material delivers a capacity of 107 mAh/g in the 4 V region, it shows excellent cyclability without any capacity loss during cycling. However, it is very interesting to see that the material in the 3 V region initially delivers
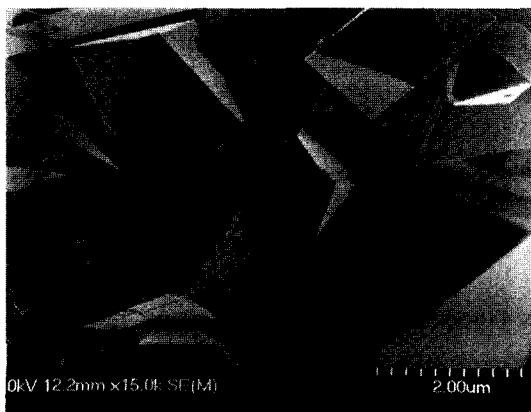

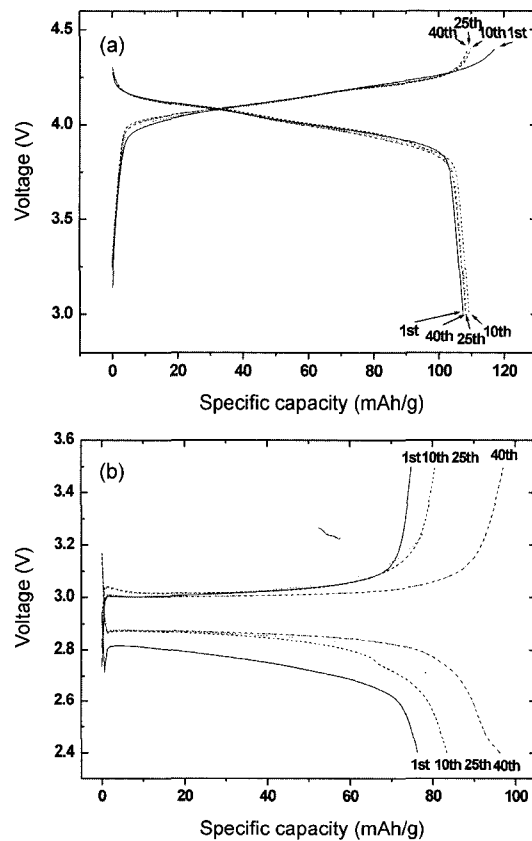**Fig. 3. Scanning electron micrographs of the $LiAl_{0.24}Mn_{1.76}O_{3.98}S_{0.02}$ powders.**

Fig. 4. Cycling charge-discharge curves for the Li/ $LiAl_{0.24}Mn_{1.76}O_{3.98}S_{0.02}$ cell in the voltage ranges of (a) 4.4~3.0 V (4 V region) and (b) 2.4~3.5 V (3 V region).

the discharge capacity of 75 mAh/g and gradually increases the capacity with cycling to reach 97 mAh/ g after the 40th cycle as shown in Fig. 2(b). It is also interesting to note that the voltage difference between the charge and discharge curves decreases during cycling. The discharge-charge behavior of the material is a unique feature contradictory to those of the stoichiometric spinel and its derivatives.

4. Summary

$LiAl_{0.24}Mn_{1.76}O_{3.98}S_{0.02}$ and $LiAl_{0.24}Mn_{1.76}O_{4.00}$ synthesized by the sol-gel method were characterized by the Rietveld refinement. They adopt the cubic spinel and its cell parameters are 8.17937(30) Å and 8.18331(19) Å respectively. There existed the distortion of the MnO_6 polyhedron with S substitu-

tion, this showed the volume change with 1.84% which can influence the capacity fading. S substitution in $LiAl_{0.24}Mn_{1.76}O_{4.00}$ also renders the capacity fading in the 3 V/4 V to decrease. It is believed that this capacity fading is connected with the distortion and volume change of the MnO_6 polyhedron.

Acknowledgment

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