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Short communication

Cycling behavior of oxysulfide spinel $\text{LiCr}_{0.19}\text{Mn}_{1.81}\text{O}_{3.98}\text{S}_{0.02}$ cathode material which shows no capacity loss in the 3-V region

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Abstract

A new oxysulfide spinel $\text{LiCr}_{0.19}\text{Mn}_{1.81}\text{O}_{3.98}\text{S}_{0.02}$ with well-developed octahedral structure is synthesized by a sol–gel method using glycolic acid as a chelating agent. The $\text{LiCr}_{0.19}\text{Mn}_{1.81}\text{O}_{3.98}\text{S}_{0.02}$ electrode shows no capacity loss in the 3- and 4-V region. This behavior is investigated by X-ray diffraction (XRD). The substitution of S for O in LiMn_2O_4 stabilizes the structural integrity of the spinel host, which in turn increases the electrochemical cycleability. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium secondary batteries; Sol–gel method; Lithium manganese oxide; Oxysulfide spinel; Jahn–Teller distortion

1. Introduction

Spinel LiMn_2O_4 and its derivatives have generated great interest as the most promising cathode materials (positive electrodes) for lithium secondary batteries due to their low cost, abundance, and non-toxicity compared with layered oxides such as LiCoO_2 and LiNiO_2 [1–4]. A significant capacity loss of the spinel LiMn_2O_4 occurs, however, during cycling and prevents its wider use as cathode material for lithium secondary batteries [5–8], especially in the 3-V region. In $\text{Li}/\text{Li}_x\text{Mn}_2\text{O}_4$ cells, when $0 \leq x \leq 1$, the cell discharges at 4 V (4-V region) versus Li/Li^+ , whereas when $1 \leq x \leq 2$, the cell discharges at 3 V (3-V region) versus Li/Li^+ [1–4]. In the 3-V region, a large capacity loss is encountered since Jahn–Teller distortion due to the reduction of the average oxidation state of Mn from 3.5 to 3.0 changes the crystal symmetry from cubic to tetragonal during Li^+ intercalation. Many research groups have improved the cycleability of LiMn_2O_4 in the 4-V region at room temperature and high temperatures, viz. such as 50–80°C by adding excess lithium, Mn-substituted stoichiometric LiMn_2O_4 spinel, anions (F, S) for O, and surface passivation treatment of LiMn_2O_4 [9–12]. There have been a few reports of cycleability in the 3-V region [7,8], but no significant improvement has been achieved.

Recently, the authors [12] reported that sulfur-doped spinel materials, i.e. oxysulfide ($\text{LiAl}_{0.24}\text{Mn}_{1.76}\text{O}_{3.98}\text{S}_{0.02}$), synthesized by a sol–gel method overcame Jahn–Teller distortion in the voltage range 2.4–4.4 V and showed excellent cycleability in the 3-V region as well as in the 4-V region [12]. The improved performance of $\text{LiAl}_{0.24}\text{Mn}_{1.76}\text{O}_{3.98}\text{S}_{0.02}$ in the 4- and 3-V regions is attributed to Al and S substitutions for Mn and O, respectively.

Here, we report the synthesis and electrochemical performance of a new spinel oxysulfide $\text{LiCr}_{0.19}\text{Mn}_{1.81}\text{O}_{3.98}\text{S}_{0.02}$, which has no capacity loss in the 3- and 4-V regions during cycling. The structural integrity of the oxysulfide material before and after the charge–discharge cycling is measured by X-ray diffraction (XRD).

2. Experimental

$\text{LiCr}_{0.19}\text{Mn}_{1.81}\text{O}_{3.98}\text{S}_{0.02}$ powders were prepared by a sol–gel method using glycolic acid as a chelating agent, see Fig. 1. $\text{Li}(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$, $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$, Li_2S , and $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (cationic ratio of $\text{Li}:\text{Mn}:\text{Li}:\text{Cr} = 0.65:1.8:0.4:0.2$) were dissolved in distilled water, and added dropwise to a continuously stirred aqueous solution of glycolic acid. The pH of the solution was adjusted to 1.5–2.0 using nitric acid to dissolve the precipitate and then to 8.5–9.0 using ammonium hydroxide. The resultant solution was evaporated at 70–80°C until a transparent sol and gel was obtained. The resulting gel precursors were

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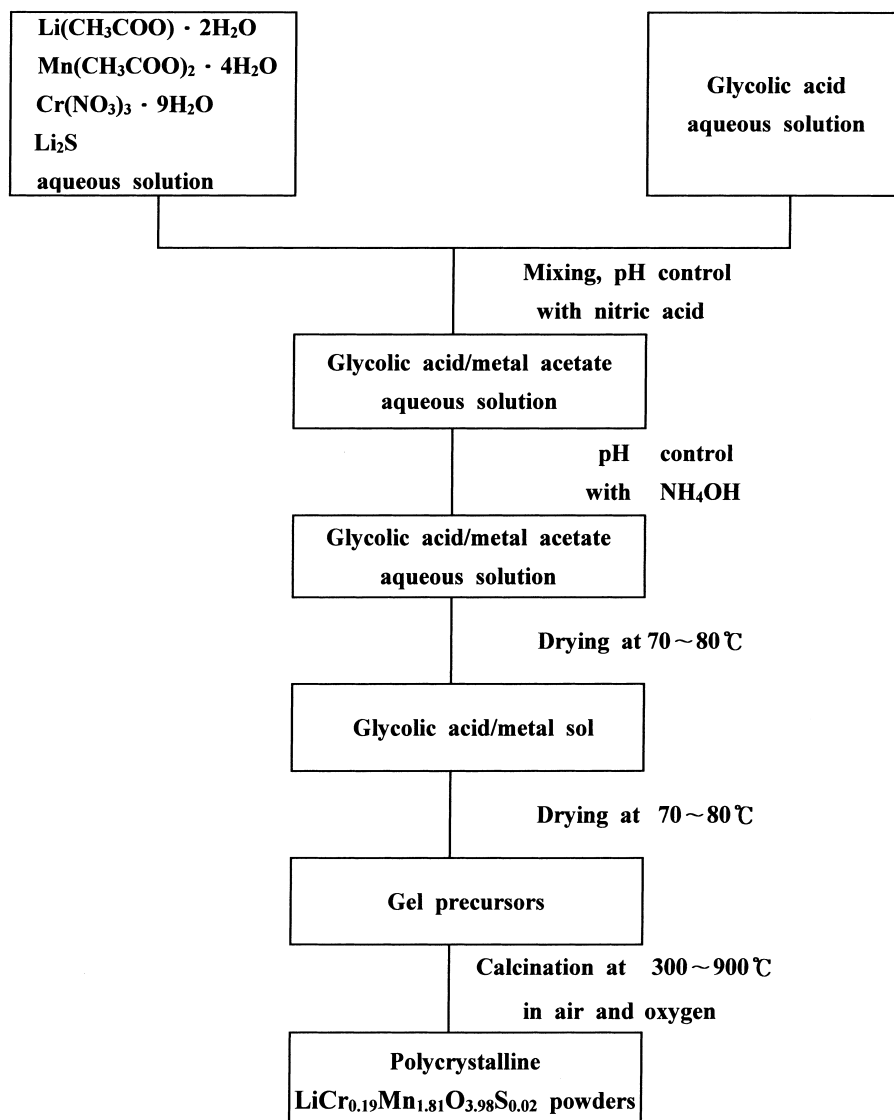


Fig. 1. Flowsheet of procedure used to prepare polycrystalline $\text{LiCr}_{0.19}\text{Mn}_{1.81}\text{O}_{3.98}\text{S}_{0.02}$ powders by sol-gel method.

decomposed at 500°C for 10 h in air, calcined at 800°C in air for 10 h, and then in flowing oxygen for 15 h.

Powder XRD (Rigaku, Rint-2000) using $\text{Cu K}\alpha$ radiation was employed to identify the crystalline phase of as-prepared powders and cycled electrodes. Rietveld refinement was then performed on the XRD data to obtain the lattice constants. Particle morphology was observed using a field emission scanning electron microscope (FE-SEM) (Hitachi Co., S-4100). The composition of lithium, aluminum and manganese was measured by means of inductively coupled plasma (ICP) by dissolving the powders in dilute nitric acid. The sulfur content was determined with a sulfur analyzer (LECO Co., CS 444) and the oxygen content was calculated by means of mass balance.

For the fabrication of the electrode, the $\text{LiCr}_{0.19}\text{Mn}_{1.81}\text{O}_{3.98}\text{S}_{0.02}$ powders were mixed with 12 wt.% carbon black and 8 wt.% polytetrafluoroethylene (PTFE), then pressed on to aluminum Exmet. Lithium foil was used as

an the negative electrode. The electrolyte was a 1:1 mixture of ethylenecarbonate (EC) and propylenecarbonate (PC) which contained 1 M LiClO_4 by volume. The charge-discharge cycle was performed galvanostatically at a current density of 0.2 mA cm^{-2} .

3. Results and discussion

Chemical analysis data show the oxysulfide sample to be $\text{LiCr}_{0.19}\text{Mn}_{1.81}\text{O}_{3.98}\text{S}_{0.02}$. XRD patterns of the as-prepared powders are given in Fig. 2. The powders are confirmed to be the well-defined spinel phase with space group $\text{Fd}3\text{m}$. The lattice constant a of the powders is 8.227 \AA , which is a much lower value than that of stoichiometric spinel [13,14].

A scanning electron micrograph (SEM) of the powders is presented in Fig. 3. The particle morphology is similar to that of single-crystal gold with a cubic structure. The

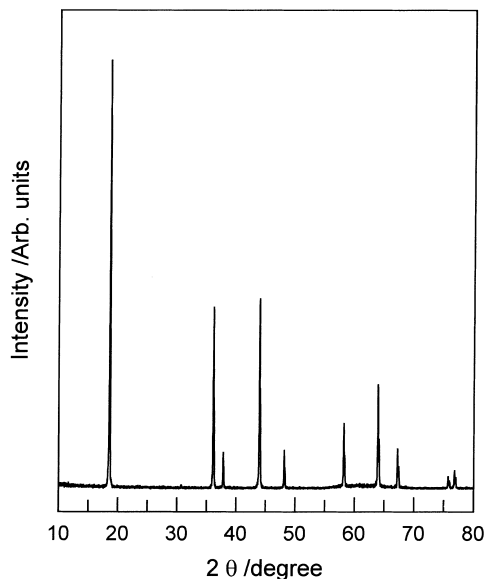


Fig. 2. XRD patterns of $\text{LiCr}_{0.19}\text{Mn}_{1.81}\text{O}_{3.98}\text{S}_{0.02}$ powder.

particles have a well-developed octahedral structure bounded by eight (1 1 1) planes. The average particle size is $3\ \mu\text{m}$ with a fairly narrow particle-size distribution.

Charge–discharge curves are given in Fig. 4 for a number of cycles in the 4- and 3-V regions at a constant current density of $0.2\ \text{mA cm}^{-2}$ at room temperature. The corresponding specific discharge capacities are shown in Fig. 5. The shape of the charge–discharge curves in the voltage range of 4.4–3.0 V exhibit two distinct potential plateaus near 4 and 4.16 V and the polarization of the electrode is almost constant during cycling, see in Fig. 4(a). Although the electrode delivers a capacity of $120\ \text{mA h g}^{-1}$, it shows excellent cycleability and retains 99% ($0.024\ \text{mA h g}^{-1}$ cycle) of the initial capacity after 50 cycles at the C/4 rate. This performance is good and competes with that of conventional materials such as LiCoO_2 and $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$. The electrochemical cycleability of the $\text{LiCr}_{0.19}\text{Mn}_{1.81}\text{O}_{3.98}\text{S}_{0.02}$ electrode was examined in the 3-V region since the stoichiometric spinel LiMn_2O_4 experience a major loss of capacity

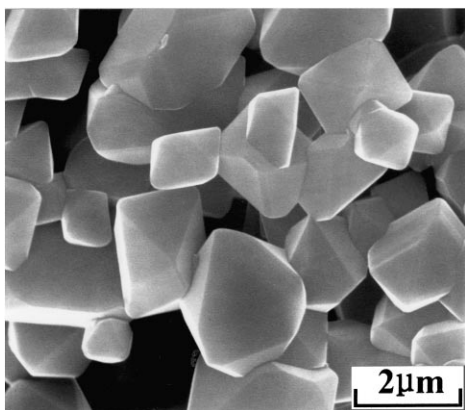


Fig. 3. Scanning electron micrograph of $\text{LiCr}_{0.19}\text{Mn}_{1.81}\text{O}_{3.98}\text{S}_{0.02}$ powder.

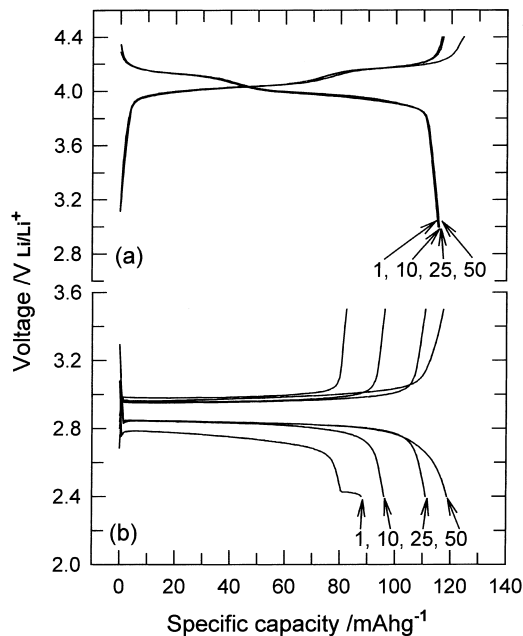


Fig. 4. Charge–discharge curves for $\text{LiCr}_{0.19}\text{Mn}_{1.81}\text{O}_{3.98}\text{S}_{0.02}/\text{Li}$ cell in voltage range: (a) 4.4–3.0 and (b) 2.4–3.5 V.

in this voltage region due to Jahn–Teller distortion. This cell was first discharged to the 2.4 V and then cycled between 3.5 and 2.4 V. Interestingly, the $\text{LiCr}_{0.19}\text{Mn}_{1.81}\text{O}_{3.98}\text{S}_{0.02}/\text{Li}$ cell initially delivers a discharge capacity of $88\ \text{mA h g}^{-1}$ which rapidly increases to $119\ \text{mA h g}^{-1}$ after 50 cycles. By contrast, it is well known that spinel suffers severe capacity loss in the 3-V region [15–17]. Thackeray et al. [16] and Huang et al. [17] have reported that the discharge capacity of stoichiometric spinel LiMn_2O_4 in the 3-V region decreases to below 50% of initial capacity during <10 cycles.

The variation of the discharge capacity in the 4-V region at various C-rates is presented in Fig. 6. The different current

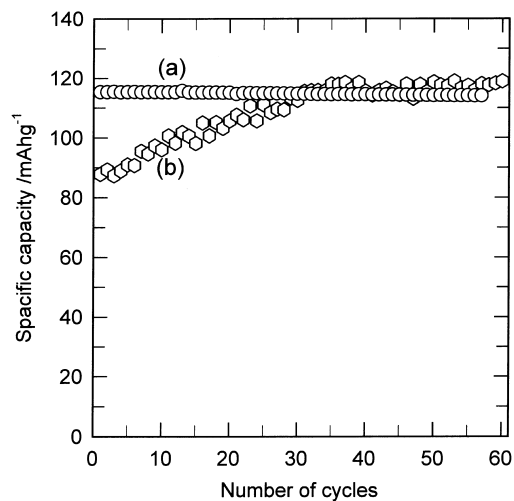


Fig. 5. Specific discharge capacities of $\text{LiCr}_{0.19}\text{Mn}_{1.81}\text{O}_{3.98}\text{S}_{0.02}/\text{Li}$ cell in (a) 4-V and (b) 3-V region as function of cycle number.

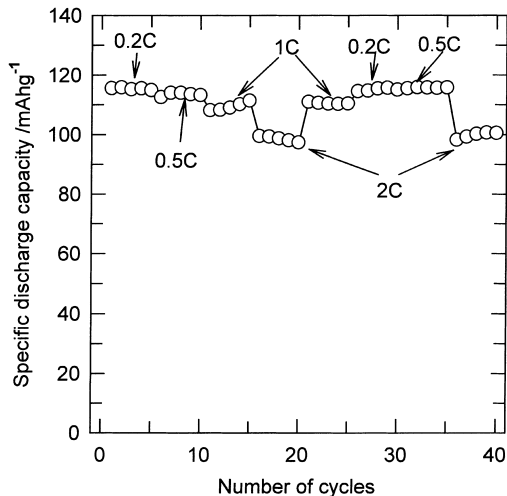


Fig. 6. Variation of specific discharge capacity as function of number of cycles for $\text{LiCr}_{0.19}\text{Mn}_{1.81}\text{O}_{3.98}\text{S}_{0.02}/\text{Li}$ cell at various C-rate.

densities were applied progressively for 5 cycles. The $\text{Li}/\text{LiCr}_{0.19}\text{Mn}_{1.81}\text{O}_{3.98}\text{S}_{0.02}$ cell displayed excellent capacity retention at all C-rates, 115 mA h g^{-1} at the 0.2 and 0.5 C-rates. The discharge capacity falls to 110 mA h g^{-1} at the 1 C-rate and 100 mA h g^{-1} at the 2 C-rate. The observed cycling stability of the $\text{LiCr}_{0.19}\text{Mn}_{1.81}\text{O}_{3.98}\text{S}_{0.02}$ could be due to a small structural transition and good contact between the positive-electrode material/PTFE/carbon interfaces during charge–discharge processing.

It is believed that the excellent cycleability of $\text{LiCr}_{0.19}\text{Mn}_{1.81}\text{O}_{3.98}\text{S}_{0.02}$ in the 4- and 3-V regions may be associated with the structural stability of the oxysulfide spinel. To understand this structural stability the electrode used to obtain the data shown in Fig. 4 (cycled the 3- and 4-V

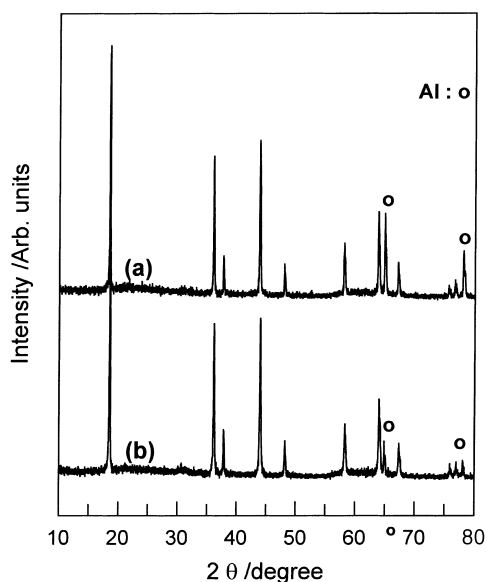


Fig. 7. XRD of $\text{LiCr}_{0.19}\text{Mn}_{1.81}\text{O}_{3.98}\text{S}_{0.02}$ electrodes cycled in voltage range: (a) 4.4–3.0 and (b) 2.4–3.5 V.

region) were characterized by XRD. The electrodes were allowed to equilibrate for 5 h in a cell at the fully discharged state and then were dried for 1 day after removal from the cell. When comparing the XRD patterns of as-prepared powders (Fig. 2) with those of $\text{LiCr}_{0.19}\text{Mn}_{1.81}\text{O}_{3.98}\text{S}_{0.02}$ (Fig. 7(a) 4.4–3.0 and (b) 2.4–3.5 V) electrodes after cycling, no difference could be found in the positions of the characteristic peaks for the typical spinel phase. This indicates that the structure of the electrode retains its original cubic spinel phase even after cycling in the 3-V region. Similar XRD data was observed for $\text{LiAl}_{0.24}\text{Mn}_{1.76}\text{O}_{3.98}\text{S}_{0.02}$ cycled in the 3-V region [12]. The lattice constants of the $\text{LiCr}_{0.19}\text{Mn}_{1.81}\text{O}_{3.98}\text{S}_{0.02}$ electrodes cycled in the 4- and 3-V regions are 8.2196 and 8.1939 Å, respectively. Considering the variation of the levels of preferred orientation in preparing the samples, it is reasonable to conclude that there is no difference in the lattice constants of the cycled electrodes.

At this stage, it is hard to explain why the oxysulfide spinel $\text{LiCr}_{0.19}\text{Mn}_{1.81}\text{O}_{3.98}\text{S}_{0.02}$ exhibits no capacity loss in the 3-V region. It should be noted, however, that the substitution of S for O is very effective in hindering the formation of the tetragonal $\text{Li}_2\text{Mn}_2\text{O}_4$ structure on the LiMn_2O_4 host in the lower voltage range [18]. Systematic experiments and characterization are in progress to explore, further the nature of the capacity stability observed here.

4. Conclusions

A new oxysulfide spinel $\text{LiCr}_{0.19}\text{Mn}_{1.81}\text{O}_{3.98}\text{S}_{0.02}$, has been synthesized by a sol–gel method using glycolic acid as a chelating agent. The $\text{LiCr}_{0.19}\text{Mn}_{1.81}\text{O}_{3.98}\text{S}_{0.02}$ electrode shows excellent cycleability with no capacity loss in the 4-V region and the discharge capacity increases during cycling in the 3-V region. XRD reveals result that the structure of the electrode retains its original cubic spinel phase, even after cycling in the 3-V region.

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