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# Cycling behavior of the oxysulfide $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$ cathode materials at elevated temperature

Yang-Kook Sun<sup>a,\*</sup>, Yung-Sung Lee<sup>b</sup>, M. Yoshio<sup>b</sup><sup>a</sup>Department of Chemical Engineering, Hanyang University, Seoul 133-791, South Korea<sup>b</sup>Department of Applied Chemistry, Saga University, Saga 840, Japan

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## Abstract

A new sulfur-doped spinel material,  $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$  was synthesized by a sol–gel method. The structural change of the oxysulfide spinel before and after cycling at elevated temperature was studied by charge–discharge measurements and X-ray diffraction. The oxysulfide spinel electrode after 50 cycles even at 50 °C shows excellent cycleability retaining 97% of the initial capacity. The capacity loss during cycling was noticeably increased in the cell operation temperature from 50 to 80 °C. The capacity loss for the spinel material,  $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$  cycled at 80 °C is attributed to the formation of tetragonal  $\text{Li}_2\text{Mn}_2\text{O}_4$  and rock salt phase  $\text{Li}_2\text{MnO}_3$ .

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## 1. Introduction

The presently commercialized lithium-ion batteries use layer-structured  $\text{LiCoO}_2$  cathode. Because of the high cost and toxicity of cobalt, an intensive search for new cathode materials has been underway in recent years. Spinel  $\text{LiMn}_2\text{O}_4$  has been considered to be attractive alternatives in terms of low cost, abundance, and nontoxicity [1–3]. The spinel  $\text{LiMn}_2\text{O}_4$  exhibits a relatively good cycleability at room temperature but still suffers from at elevated temperature, e.g. 50–80 °C [4,5]. In order to improve the cycleability of spinel  $\text{LiMn}_2\text{O}_4$  electrodes at elevated temperature, many research groups have been studied the modification

of the  $\text{LiMn}_2\text{O}_4$  by lithium rich or transition metal-doped spinel, by reducing surface reaction between spinel electrode and electrolyte, by F partial substitution for O, by sol–gel coating of  $\text{LiCoO}_2$  [6–9]. Although some attempts have some improved the electrochemical performance of spinel  $\text{LiMn}_2\text{O}_4$  electrode at elevated temperature, the capacity loss was still observed during cycling.

The reason for the capacity loss of the  $\text{LiMn}_2\text{O}_4$  is mainly attributed to a slow dissolution of MnO at the spinel electrode into electrolyte due to the formation of HF resulting from the reaction of  $\text{LiPF}_6$  with residual  $\text{H}_2\text{O}$  [10]. However, there is not yet explicit degradation mechanism of the spinel  $\text{LiMn}_2\text{O}_4$  electrode at elevated temperature.  $\text{Li}_x\text{Mn}_2\text{O}_4$  ( $x=1$ ) has a cubic spinel structure with space group symmetry  $Fd3m$  in which the  $\text{Li}^+$  and  $\text{Mn}^{3+/4+}$  ions are located on the 8a tetrahedral sites and the 16d octahedral sites of the

\* Corresponding author. Tel.: +82-2-2290-0524; fax: +82-2-2282-7329.

E-mail address: yksun@hanyang.ac.kr (Y.-K. Sun).

structure, respectively [1,11]. Thackeray et al. [12] have proposed a failure mechanism at room temperature that a tetragonal  $\text{Li}_2\text{Mn}_2\text{O}_4$  phase has been detected by TEM diffraction image at the surface of discharged  $\text{Li}_x\text{Mn}_2\text{O}_4$  spinel electrodes cycled under high rate, nonequilibrium conditions between 4.2 and 3.3 V. The presence of  $\text{Li}_2\text{MnO}_3$  and spinel compositions other than  $\text{LiMn}_2\text{O}_4$  in cycled  $\text{Li}_x\text{Mn}_2\text{O}_4$  electrodes has been reported previously by Robertson et al. [13]. It was subsequently suggested by Cho and Thackeray [14] that a capacity fade for  $\text{LiMn}_2\text{O}_4$  electrode cycled hundreds of times at room temperature is attributed to the formation of  $\text{Li}_2\text{MnO}_3$  caused by the dissolution of MnO from the previously formed  $\text{Li}_2\text{Mn}_2\text{O}_4$ .

$\text{LiMn}_2\text{O}_4$  powders are typically prepared by a solid-state reaction that consists of extensive mechanical mixing and extended grinding process. This method, however, has several disadvantages; inhomogeneity, irregular morphology, broader particle size distribution, and long and repeated heat treatment processes. Employing a sol–gel method has solved these difficulties. All the components derived from the gel precursors are of atomic scale and homogeneously mixed with each other, and thus form a single phase spinel  $\text{LiMn}_2\text{O}_4$  having submicron, narrow particle size distribution, and excellent phase-pure particles under the mild conditions. For this reason, we have adopted the sol–gel method using various kinds of chelating agent to synthesize several cathode materials [15–18].

In this paper, we study the electrochemical cycling behavior of a new oxysulfide spinel  $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$  materials at elevated temperature (50–80 °C) combined with the structural degradation. X-ray diffraction (XRD) and charge–discharge measurements were used to investigate the cycling induced phase transformation of the spinel electrode.

## 2. Experimental

$\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$  powders were prepared by a sol–gel method as reported in our previous works [13,15].  $\text{Li}_{1.06}\text{Al}_{0.2}\text{Mn}_{1.8}\text{O}_{3.8}\text{S}_{0.2}$  was a starting composition of  $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$ . The slight excess of Li was introduced to compensate for loss during high-temperature calcination. Powder X-ray

diffraction (Rigaku, Rint-2000) using  $\text{CuK}\alpha$  radiation was used to identify the crystalline phase of cycled electrodes at various temperature. The contents of lithium, aluminum, and manganese were measured using the inductively coupled plasma (ICP) method by dissolving the powders in dilute nitric acid. The sulfur was analyzed with a sulfur analyzer (LECO, CS 444), and the oxygen content was determined via mass balance. The particle morphology of  $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$  powders was observed using a field emission scanning electron microscope (Hitachi, S-4100). We prepared the XRD sample of the cycled  $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$  electrode as follows: the  $\text{Li}/\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$  cell discharged to 3.0 V was allowed to equilibrate for 5 h at each operating temperature. After cooling the cell down to room temperature, the  $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$  electrode was removed from the cell and then dried for 1 day.

Charge–discharge cycling was performed in CR2032 button 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  $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$  powders and 15 mg conducting binder (10 mg TAB and 5 mg graphite), was pressed on 2.0-cm<sup>2</sup> stainless screen at 800 kg cm<sup>−2</sup>. The used electrolyte was a 1:2 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) containing 1 M  $\text{LiPF}_6$  by volume. The charge–discharge cycle was performed galvanostatically at a current rate of  $C/3$  (0.4 mA cm<sup>−2</sup>) between 4.4 and 3.0 V.

## 3. Results and discussion

The as-prepared powders were confirmed to be well-defined spinel phase with space group  $Fd3m$  shown in Fig. 1. The lattice constant ( $a$ ) of the powders is 8.1963 Å, which is lower than that of stoichiometric spinel [2]. Generally, spinels with smaller lattice constant showed improved cycleability. Amatucci et al. [19] have reported that  $\text{LiAl}_{0.2}\text{Mn}_{1.8}\text{O}_4$  prepared by solid-state techniques had a lattice constant of 8.20 Å and it showed a much improved cycleability at elevated temperature as well as room temperature compared with stoichiometric spinel  $\text{LiMn}_2\text{O}_4$ . The solid solution range of Al-doped  $\text{LiMn}_2\text{O}_4$  spinel synthesized by emulsion drying method was in the range of

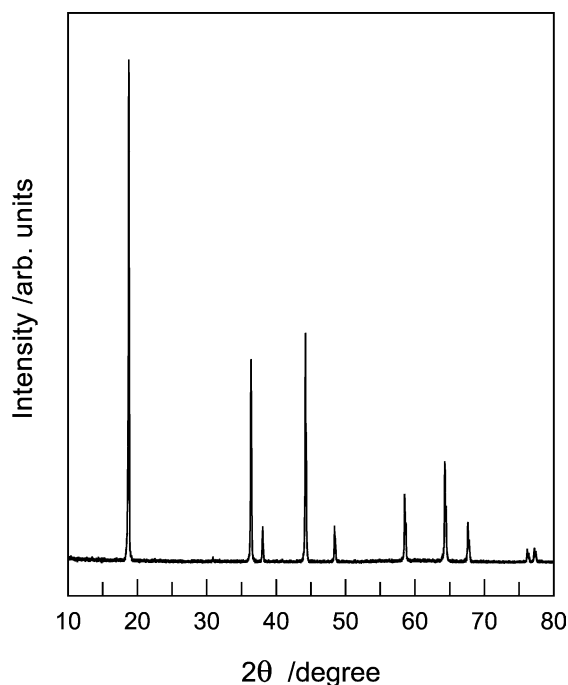


Fig. 1. X-ray diffraction patterns for  $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$  powders.

$x=0-0.6$  in  $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$  and the lattice constant linearly decreased from 8.245 Å at  $x=0$  to 8.136 Å at  $x=0.6$  [20]. The chemically analyzed data showed that the powder composition was  $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$ .

Fig. 2 shows scanning electron microscope (SEM) for the as-prepared powders. The particles have a

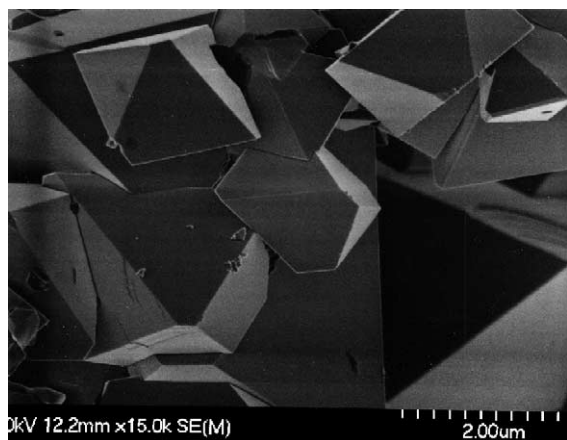


Fig. 2. Scanning electron micrographs of the  $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$  powders.

single crystal-like gold with cubic structure shapes. They are quite different in particle morphology from the stoichiometric spinel with a well-developed (100) plane and have the particle size distribution of 1–10 μm.

Fig. 3 shows the charge–discharge curves for the  $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$  electrode at 25, 50, and 80 °C. The charge–discharge curves have only one plateau due to a large amount of Al substitution for Mn, which could be ascribed to a single phase reaction in the voltage region. Xia et al. [5,7] reported

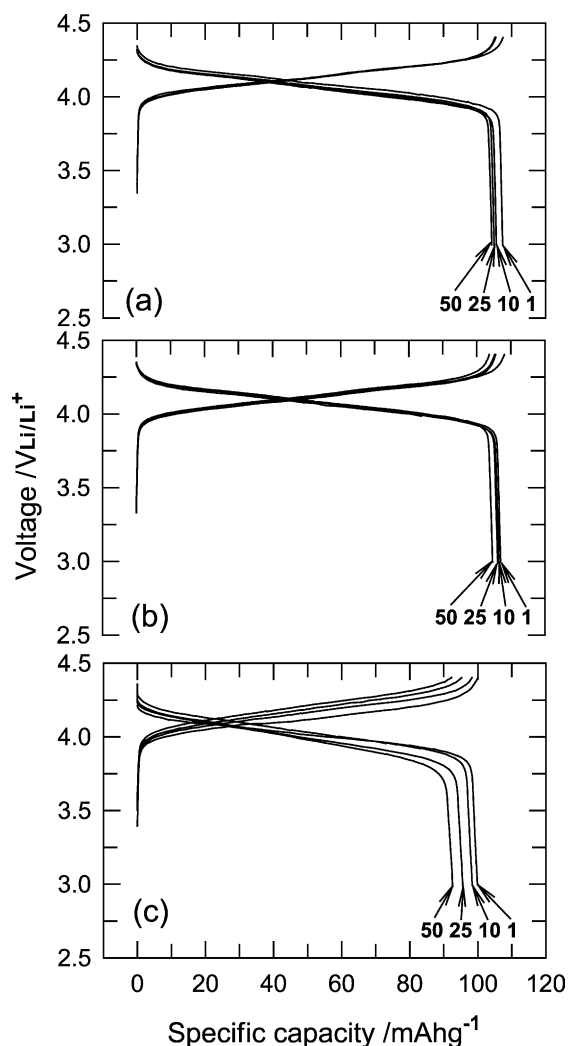


Fig. 3. Charge–discharge curves for  $\text{Li}/\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$  cells at (a) 25, (b) 50, and (c) 80 °C as a function of cycle number.

that the spinel having one-phase reaction during charge–discharge cycling showed better cycleability. The voltage difference between the charge and discharge curves for the  $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$  electrode cycled at 80 °C increases with increasing cycle number, whereas there is no difference in the charge–discharge curves for the  $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$  electrode cycled at 25 and 50 °C. It is postulated by these results that the capacity loss at elevated temperature during cycling is related to the structural degradation of the  $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$  host resulted from MnO dissolution. Shown in Fig. 4 is the variation of specific discharge capacity for the oxysulfide spinel electrode during cycling at various temperatures. Although the electrode cycled at 25 °C (Fig. 4(a)) delivers an initial capacity of 107 mA h g<sup>-1</sup>, it shows excellent rechargeability retaining 97% of the initial capacity after 50 cycles at C/3 rate. It is noticeable that 3% capacity loss for the  $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$  electrode after 50 cycles even at 50 °C is observed, which is the same capacity loss of the 0.05 mA h g<sup>-1</sup>·cycle for the electrode cycled at 25 °C. However, Li/LiAl<sub>0.18</sub>Mn<sub>1.82</sub>O<sub>3.97</sub>S<sub>0.03</sub> cell cycled at 80 °C initially delivers the discharge capacity of 100 mA h g<sup>-1</sup> and decrease slowly during cycling to reach 93

mA h g<sup>-1</sup> after 50 cycles with capacity retention of 93% of the initial capacity (capacity loss of 0.134 mA h g<sup>-1</sup>·cycle), which is the lowest capacity loss reported to so far. It should be noted that the capacity loss at 80 °C is much higher than that at 25 and 50 °C. Myung et al. [20] reported that the  $\text{LiAl}_{0.3}\text{Mn}_{1.7}\text{O}_4$  electrodes synthesized by the emulsion drying method suffered from capacity loss of 98 and 95% after 50 cycles at 25 and 45 °C, respectively. The excellent capacity retention of  $\text{LiAl}_{0.15}\text{Mn}_{1.85}\text{O}_{3.97}\text{S}_{0.03}$  spinel electrode at the elevated temperature is largely due to the smaller lattice constant, an increase in covalency by Al substitution, and excellent homogeneity of powders synthesized by a sol–gel method. Recently, Gee et al. [21] reported that an increase in covalent or metallic bonding play an important role in suppressing Jahn–Teller distortion in spinel  $\text{LiMn}_2\text{O}_4$  phase. The above results indicate that our prepared oxysulfide manganese oxides are a good cathode material, which can compete with the conventional cathode materials such as  $\text{LiCoO}_2$  and  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  for the application of the high-temperature performance of lithium batteries. This oxysulfide spinel oxide is an attractive cathode material for lithium secondary batteries due to the temperature stability and excellent electrochemical performance as well as the nontoxicity and low cost of the raw materials.

The capacity loss during cycling has been commonly considered to be due to the MnO dissolution into the electrolyte solution. In order to study the structural change of spinel  $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$  electrode induced by Mn dissolution after cycling at elevated temperature, XRD measurements were carried out. Fig. 5 shows the X-ray diffraction patterns of the  $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$  electrodes after 50 cycles at 25, 50, and 80 °C. For the cycled spinel electrodes at 25 and 50 °C, no impurity phases have been observed after 50 cycles. But the X-ray diffraction patterns of the spinel materials cycled (Fig. 5(a) and (b)) shift slightly to the right, indicating that a contraction of lattice constant and a change of composition of the spinel component compared with those of the as-prepared powders (Fig. 1) [10]. A small amount of peaks that could be indexed to  $\text{Li}_2\text{Mn}_2\text{O}_4$  with tetragonal and  $\text{Li}_2\text{MnO}_3$  with rock salt phase appeared for the cycled electrode at 80 °C (Fig. 5(c)). The existence of those phases are mainly related to the

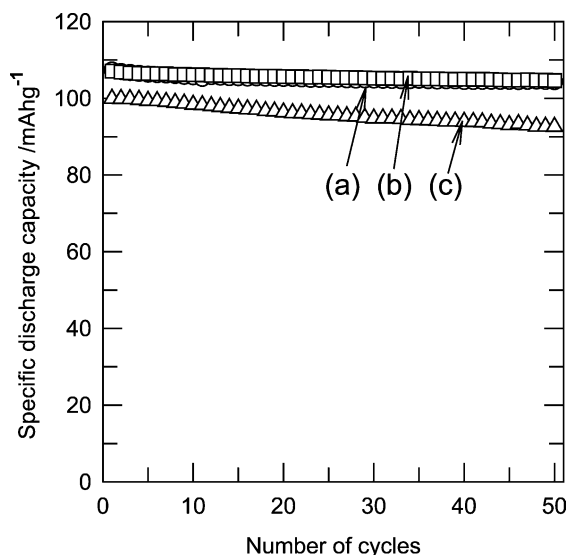


Fig. 4. Specific discharge capacity for the  $\text{Li/LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$  cell as a function of cycle number at (a) 25 °C, (b) 50 °C, and (c) 80 °C.

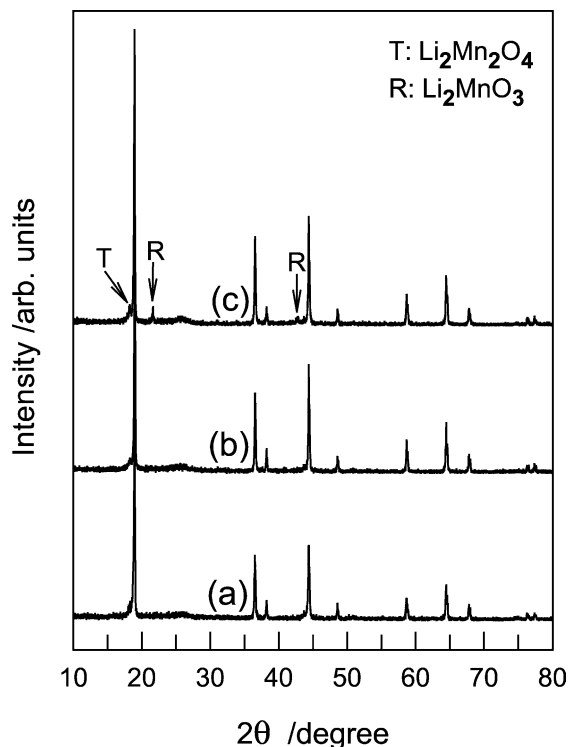


Fig. 5. X-ray diffraction patterns for  $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$  electrodes after 50 cycles (a) 25 °C, (b) 50 °C, and (c) 80 °C.

capacity loss for the spinel electrode cycled at 80 °C. Recently, Cho and Thackeray [14] reported that the  $\text{Li}_2\text{MnO}_3$  concentration increased with cycling, reached a maximum after 220 cycles, and decreased to 500 cycles, whereas  $\text{Li}_2\text{Mn}_2\text{O}_4$  peaks increased with cycling and disappeared after 220 cycles. The rock salt phase  $\text{Li}_2\text{MnO}_3$  has been detected in a very minor amount by HRTEM lattice image at the particle surface of discharged spinel electrode after 70 cycling at 80 °C, which is mainly responsible to the origin of capacity loss [22]. Our data confirm the above observations.

From the above results, the small capacity loss in  $\text{Li}/\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$  cell at elevated temperature is ascribed to a structural degradation of the spinel electrode and which is associated with the formation of  $\text{Li}_2\text{Mn}_2\text{O}_4$  and  $\text{Li}_2\text{MnO}_3$ . It is concluded that the formation of  $\text{Li}_2\text{MnO}_3$  is attributed to the dissolution of MnO from  $\text{Li}_2\text{Mn}_2\text{O}_4$ , which have been formed at the surface of discharged  $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$  electrode.

#### 4. Conclusions

A new oxysulfide spinel,  $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$  electrode cycled at elevated temperature shows excellent cycleability at a high rate over the 4 V region. The capacity retentions of the oxysulfide electrode after 50 cycles at 25, 50, and 80 °C are 97%, 97%, and 95% of initial capacity, respectively. The  $\text{Li}_2\text{Mn}_2\text{O}_4$  with tetragonal and  $\text{Li}_2\text{MnO}_3$  with rock salt phase was detected at the surface of discharged electrode after 50 cycles at 80 °C, which was the main origin of the capacity loss of the spinel electrode at elevated temperature.

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