

Electrochemical Properties of the Oxsulfide $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$ Cathode Materials at Elevated Temperature

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Abstract—A 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 using glycolic acid as chelating agent. 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 capacity loss during cycling was noticeably increased in the cell operation temperature from 50 to 80 °C. The capacity loss for the spinel material during cycling at elevated temperature is largely attributed to the formation of tetragonal $\text{Li}_2\text{Mn}_2\text{O}_4$ and rock salt phase Li_2MnO_3 .

Key words: Lithium-Ion Battery, Sol-Gel Method, Al Doping, Sulfur Doping, High Temperature

INTRODUCTION

The presently commercialized lithium-ion batteries use layer structured 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 LiMn_2O_4 has been considered to be an attractive alternative in terms of low cost, abundance, and nontoxicity [Amine, 1996]. The spinel LiMn_2O_4 exhibits a relatively good cycle-ability at room temperature but still suffers from capacity loss at elevated temperature, e.g. 50–80 °C [Amatucci, 1997; Xia, 1997]. In order to improve the cycle-ability of spinel LiMn_2O_4 electrodes at elevated temperature, many research groups have studied the modification of the LiMn_2O_4 by lithium rich or transition metal doped spinel, by reducing surface reaction between spinel electrode and electrolyte, by F partial substitution for O, and by sol-gel coating of LiCoO_2 [Amatucci, 1997; Xia, 2000; Cho, 1999]. Although some attempts have somewhat improved the electrochemical performance of spinel LiMn_2O_4 electrode at elevated temperature, capacity loss has still been observed during cycling.

The reason for the capacity loss of the LiMn_2O_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 LiPF_6 with residual H_2O [Pasquier, 1999]. However, there is not yet an explicit degradation mechanism of the spinel LiMn_2O_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 $\text{Fd}\bar{3}\text{m}$ 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 [Pasquier, 1999]. Thackeray et al. have proposed a failure mechanism at room temperature in which 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

[Thackeray, 1998]. The presence of Li_2MnO_3 and spinel compositions other than LiMn_2O_4 in cycled $\text{Li}_x\text{Mn}_2\text{O}_4$ electrodes has been reported previously by Robertson and co-workers [Robertson, 1997]. It was subsequently suggested that a capacity fade for LiMn_2O_4 electrode cycled hundreds of times at room-temperature is attributed to the formation of Li_2MnO_3 caused by the dissolution of MnO from the previously formed $\text{Li}_2\text{Mn}_2\text{O}_4$ [Cho, 1999].

LiMn_2O_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 LiMn_2O_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 [Sun, 1997, 1999; Park, 2000].

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.

EXPERIMENTAL SECTION

$\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$ powders were prepared by a sol-gel method as reported in our previous works [Sun, 2001]. $\text{Li}_{1.06}\text{Al}_{0.2}\text{Mn}_{1.8}\text{O}_{3.8}\text{S}_{0.2}$ 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 temperatures. The contents of lithium, aluminum, and manganese were measured by using the inductively

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[†]This paper is dedicated to Professor Wha Young Lee on the occasion of his retirement from Seoul National University.

coupled plasma (ICP) method by dissolving the powders in dilute nitric acid. The sulfur was analyzed with a sulfur analyzer (LECO Co., 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 by using a field emission scanning electron microscope (Hitachi Co., 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 the cell was cooled 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 one 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^2 stainless screen at 800 kg cm^{-2} . The used electrolyte was a 1 : 2 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) containing 1 M LiPF_6 by volume. The charge-discharge cycle was performed galvanostatically at a current rate of C/3 (0.4 mA cm^{-2}) between 4.4 and 3.0 V.

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 \AA which is lower than that of stoichiometric spinel. Generally, spinels with smaller lattice constant showed improved cycle-ability. Amatucci et al. 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 \AA and it showed much improved cycle-ability at elevated temperature as well as room temperature compared with stoichiometric spinel LiMn_2O_4 [Amatucci, 2001]. The solid-solution

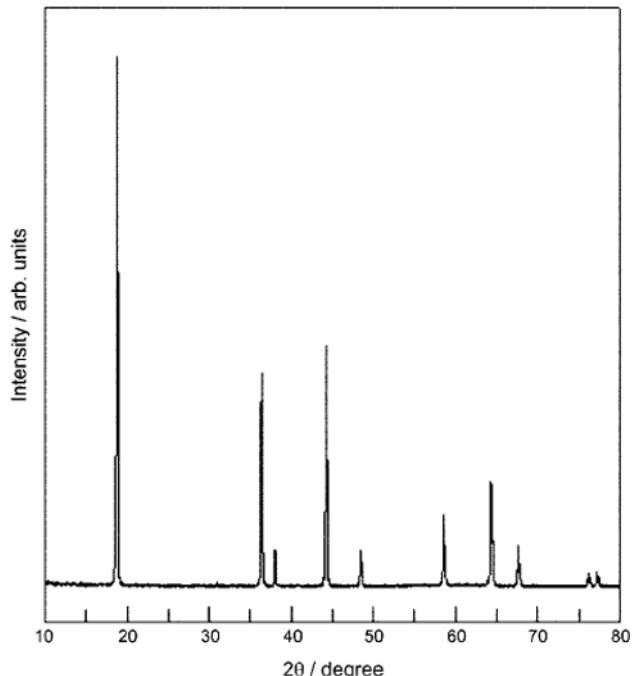


Fig. 1. X-ray diffraction patterns for $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$ powders.

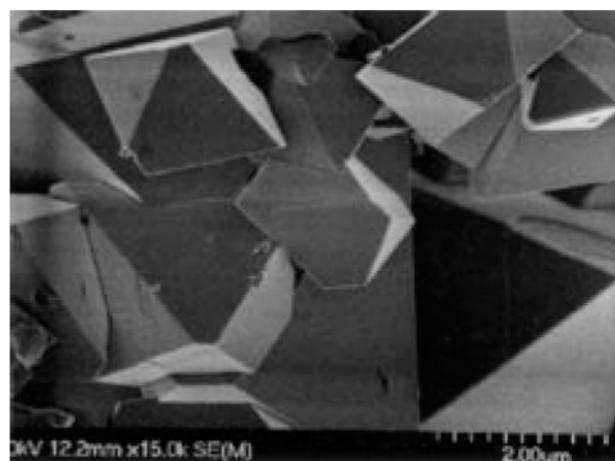


Fig. 2. Scanning electron micrographs of the $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$ powders.

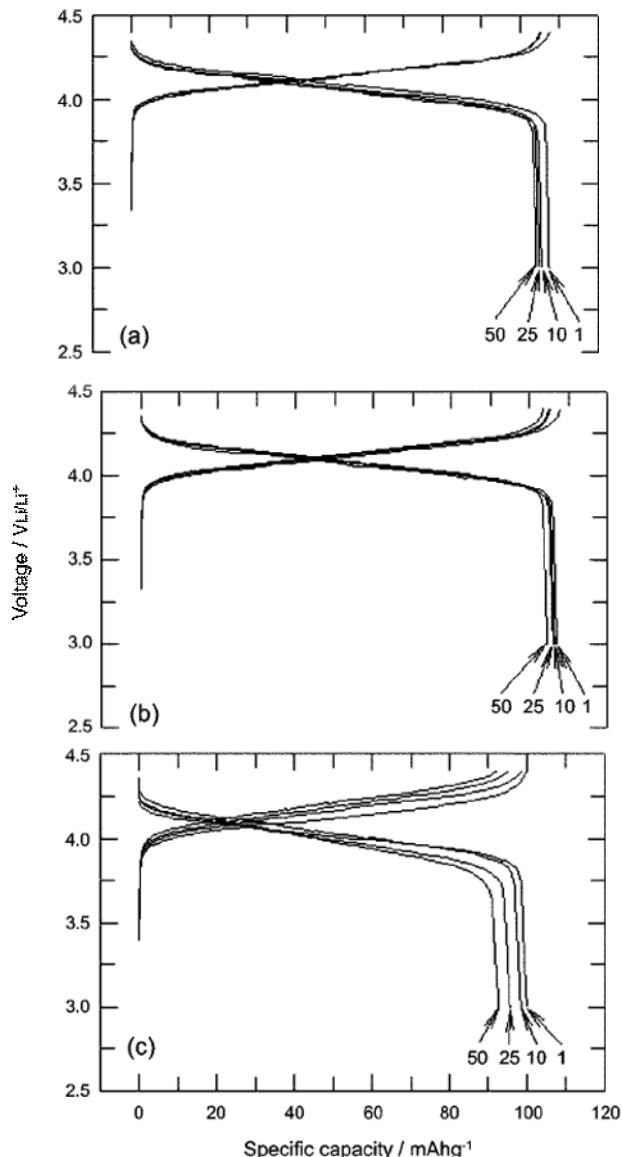


Fig. 3. Charge-discharge curves for $\text{Li}/\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$ cells at (a) 25, (b) 50, and (c) 80°C as a function of cycle number.

range of Al doped LiMn_2O_4 spinel synthesized by emulsion drying method was in the range of $x=0\text{--}0.6$ in $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$ and the lattice constant linearly decreased from 8.245 \AA at $x=0$ to 8.136 \AA at $x=0.6$ [Myung, 2001]. 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 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 $1\text{--}10\text{ }\mu\text{m}$.

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 and co-workers reported that the spinel having one-phase reaction during charge-discharge cycling showed better cyclability [Amatucci, 1997]. 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 resulting 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^{-1} , 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 $0.05\text{ mA h g}^{-1}\text{-cycle}$ for the electrode cycled at 25 °C. However, the $\text{Li/LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$ cell which cycled at 80 °C initially deliv-

ered the discharge capacity of 100 mA h g^{-1} and decreased slowly during cycling to reach 93 mA h g^{-1} after 50 cycles with capacity retention of 93% of the initial capacity (capacity loss of $0.134\text{ mA h g}^{-1}\text{-cycle}$), 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. 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 [Myung, 2001]. 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 covalence by Al substitution, and excellent homogeneity of powders synthesized by a sol-gel method. Recently, Gee et al. reported that an increase in covalent or metallic bonding plays an important role in suppressing Jahn-Teller distortion in spinel LiMn_2O_4 phase [Gee, 1998]. 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 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

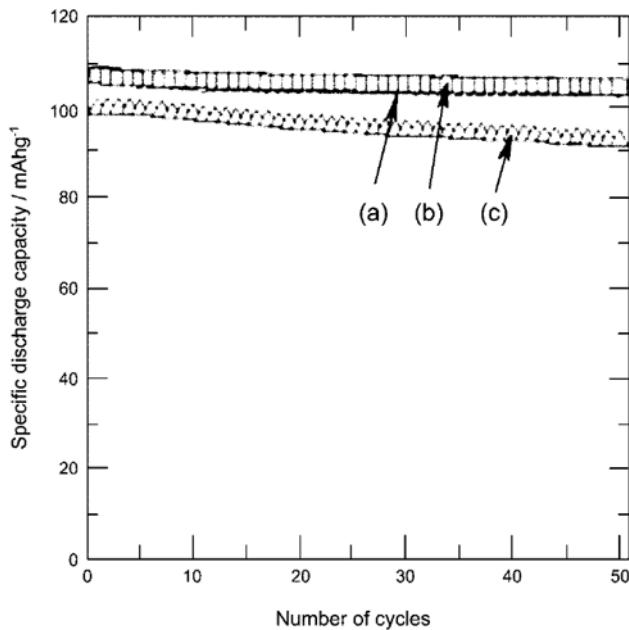


Fig. 4. Specific discharge capacity for the $\text{Li/LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$ cell as a function of cycle number at (a) 25, (b) 50 °C, and (c) 80 °C.

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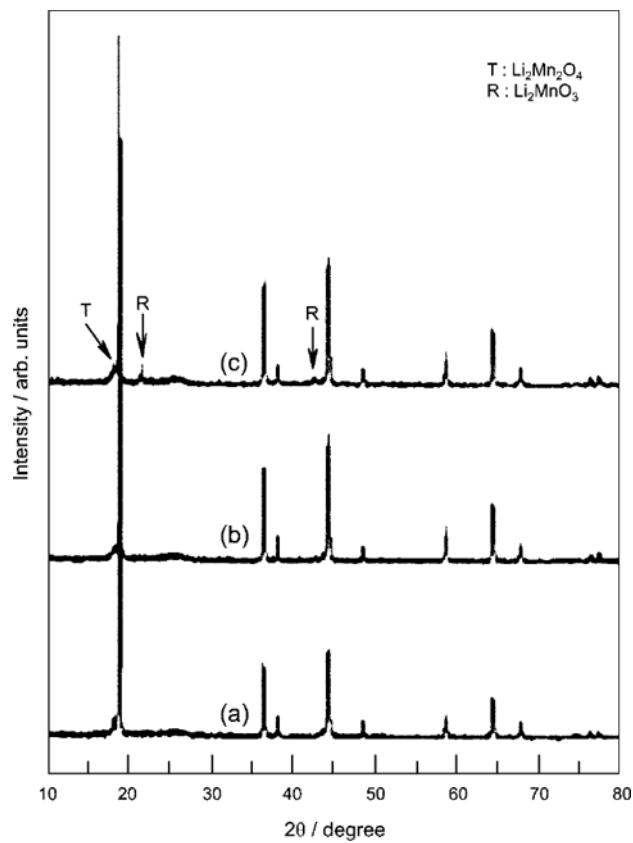


Fig. 5. X-ray diffraction patterns for $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$ electrodes after 50 cycles (a) 25, (b) 50, and (c) 80 °C.

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) [Pasquier, 1999]. A small amount of peaks that could be indexed to $\text{Li}_2\text{Mn}_2\text{O}_4$ with tetragonal and Li_2MnO_3 with rock salt phase appeared for the cycled electrode at 80 °C [Fig. 5(c)]. The existence of those phases is mainly related to the capacity loss for the spinel electrode cycled at 80 °C. Recently, it was reported that the Li_2MnO_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 [Pasquier, 1999]. The rock salt phase Li_2MnO_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 for the origin of capacity loss [Sun et al., 2001]. Our data confirms 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, which is associated with the formation of $\text{Li}_2\text{Mn}_2\text{O}_4$ and Li_2MnO_3 . It is concluded that the formation of Li_2MnO_3 is attributed to the dissolution of MnO from $\text{Li}_2\text{Mn}_2\text{O}_4$ which has been formed at the surface of discharged $\text{LiAl}_{0.18}\text{Mn}_{1.82}\text{O}_{3.97}\text{S}_{0.03}$ electrode.

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. $\text{Li}_2\text{Mn}_2\text{O}_4$ with tetragonal and Li_2MnO_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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