

# Nickel Chevrel-phase sulfides $\text{Ni}_y\text{Mo}_6\text{S}_{8-z}$ and $\text{Ni}_y\text{Mo}_6\text{S}_{8-z}\text{O}_n$ as the cathode of lithium secondary batteries

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## Abstract

As cathode of lithium secondary batteries, some nickel Chevrel-phase sulfides (NMS:  $\text{Ni}_y\text{Mo}_6\text{S}_{8-z}$ ) with nonstoichiometric compositions both in nickel and sulfur were reexamined, and their promising cycling properties at ambient temperature were recognized. The Li/NMS cells could be galvanostatically discharged up to  $x=4$  ( $\text{Li}_x\text{NMS}$ ) when the current density was  $0.5 \text{ mA/cm}^2$ . Also the NMS which partly incorporated oxygen in the cluster structure (NMSO: e.g.,  $\text{Ni}_2\text{Mo}_6\text{S}_{7.5}\text{O}_{0.1}$ ) were tested as the cathode of lithium secondary batteries. In a deep cycling test carried out between 1.5 and 2.7 V for NMS and NMSO, more than 50% of the initial discharge capacity was maintained at the 60th cycle. NMSO cathode at the composition  $\text{Ni}_2\text{Mo}_6\text{S}_{7.5}\text{O}_{0.1}$  showed more excellent discharge/charge cycling properties than those in NMS.

## Introduction

A large number of chalcogenides with three-dimensional frameworks, e.g., molybdenum cluster sulfides,  $\text{M}_y\text{Mo}_6\text{S}_{8-z}$  (Chevrel-phases,  $\text{M} = \text{metal}$ ), have been examined as cathode material, at room temperature, in organic electrolyte lithium secondary batteries [1-5]. Lithium ions are reversibly inserted in the structural vacant sites (A (inner) and B (outer) sites [6]) of these host materials. Recently, we have determined the single phase region of  $\text{Ni}_y\text{Mo}_6\text{S}_{8-z}$  (NMS) at  $1000^\circ\text{C}$  [7], and the discharge/charge cycling properties of some nonstoichiometric NMS showed good performance [5, 7]. Also no metallic nickel deposition was observed in the cathode even after hundreds of cycles.

On the other hand, some Chevrel-phase sulfides incorporate oxygen in the structure [8, 9]. In a preliminary experiment, we have found that NMS also incorporate small amounts of oxygen in the cluster structure and form  $\text{Ni}_y\text{Mo}_6\text{S}_{8-z}\text{O}_n$  (NMSO). It is expected that NMSO increase the structural stability by the incorporation of oxygen because of higher electronegativity of oxygen (3.5) than that of sulfur (2.5) and lead to improve the cycles.

In the present paper, the effect of the concentration of both nickel and sulfur in NMS for discharge/charge cycling properties will be reexamined. Also the cell properties of NMSO will be discussed in comparison with those of NMS at room temperature.

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## Experimental

NMS were prepared from their elements in an evacuated silica capsule. The capsule was heated first at 1000 °C for two days, followed by regrinding the resultant compound and then by heating at the same temperature in the silica capsule for another three days. NMSO were prepared by reacting NMS with 0.15% NO-He mixed gas at 300 °C for 12–24 h, according to our method described in ref. 10. The amount of oxygen was calculated from weight changes before and after the reaction.  $\text{Ni}_2\text{Mo}_6\text{-S}_{7.5}\text{O}_{0.05}$  was prepared by heating  $\text{Ni}_2\text{Mo}_6\text{S}_{7.5}$  for 12 h, and  $\text{Ni}_2\text{Mo}_6\text{-S}_{7.5}\text{O}_{0.1}$  was obtained by heating  $\text{Ni}_2\text{Mo}_6\text{S}_{7.5}$  for 24 h. The hexagonal lattice parameter changes of NMS and NMSO were calculated from X-ray diffraction pattern using Cu  $K\alpha$  radiation.

The galvanostatic measurement of a lithium rechargeable cell is almost the same as that described earlier [3, 5, 7]. No cathode additive, like a graphite, was used in the present study because of metallic conduction of NMS and NMSO.

## Results and discussion

The crystal structure of the Chevrel-phase sulfides with smaller M atoms, e.g., Fe, Ni and Cu, is illustrated in Fig. 1 with unit cells of hexagonal crystal lattice. This illustration has been drawn on the basis of the Cu, Mo, and S positions in  $\text{Cu}_3\text{Mo}_6\text{S}_8$  [11]. Nickel atoms partially occupy the 12 metal sites which are located between two  $\text{Mo}_6\text{S}_8$  clusters neighboring along the hexagonal  $c$ -axis ( $\bar{3}$ -axis) (Fig. 1(b)). Lithium atoms intercalated in the structure by a discharge reaction also enter into some of these residual vacant metal sites. The hexagonal lattice parameters of  $\text{Ni}_2\text{Mo}_6\text{S}_{7.5}\text{O}_n$

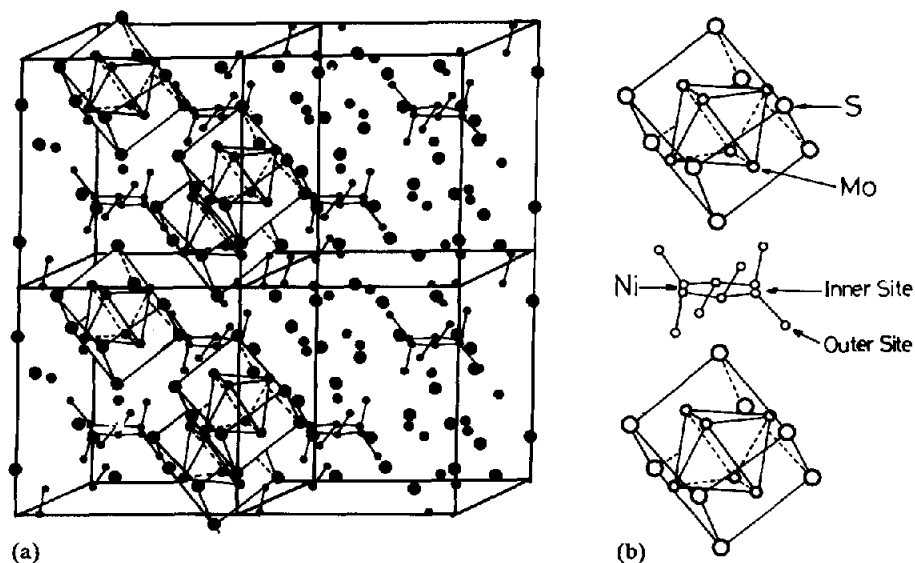


Fig. 1. (a) Crystal structure of Chevrel-phase sulfides with hexagonal unit cells, and (b) inner and outer nickel metal sites between two  $\text{Mo}_6\text{S}_8$  clusters.

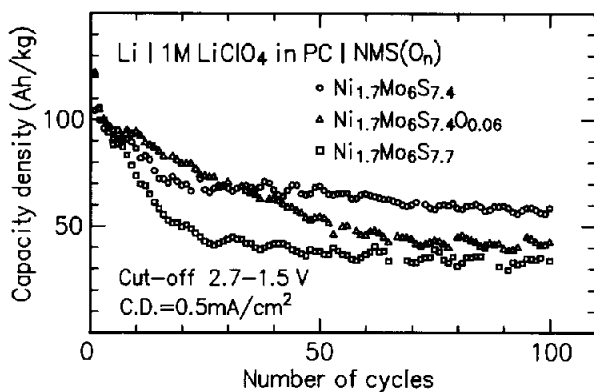
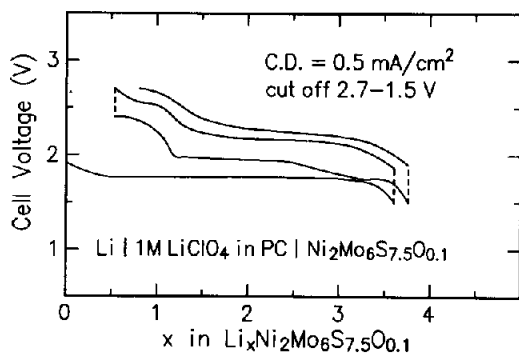
are summarized in Table 1. No remarkable change in lattice parameters could be found after the incorporation of oxygen in the structure. So far, we do not know the detailed position of the oxygen in the cluster structure.

Figure 2 shows the relationship between capacity density and cycles of NMS and NMSO in the composition of  $\text{Ni}_{1.7}\text{Mo}_6\text{S}_{7.4}$  and of  $\text{Ni}_{1.7}\text{Mo}_6\text{S}_{7.7}$ . Since the current density of NMS in the present study ( $0.5 \text{ mA/cm}^2$ ) was one half of the previous study [7], the capacity density for cycling was improved in the present experiment. The vacant sites of sulfur would make an easier intercalation and deintercalation of lithium ions without any serious structural hindrance, because the cyclic behavior of  $\text{Ni}_{1.7}\text{Mo}_6\text{S}_{7.4}$  was better than that of  $\text{Ni}_{1.7}\text{Mo}_6\text{S}_{7.7}$ . Figure 3 shows deep cycling behavior of

TABLE 1

Hexagonal lattice parameters of  $\text{Ni}_2\text{Mo}_6\text{S}_{7.5}\text{O}_n$ 

Chevrel-phase sulfides	$a$ (Å)	$c$ (Å)
$\text{Ni}_2\text{Mo}_6\text{S}_{7.5}$	9.524	10.247
$\text{Ni}_2\text{Mo}_6\text{S}_{7.5}\text{O}_{0.05}$	9.525	10.245
$\text{Ni}_2\text{Mo}_6\text{S}_{7.5}\text{O}_{0.1}$	9.523	10.253

Fig. 2. Capacity density vs. cycle number for  $\text{Ni}_{1.7}\text{Mo}_6\text{S}_{7.7}$ ,  $\text{Ni}_{1.7}\text{Mo}_6\text{S}_{7.4}$  and  $\text{Ni}_{1.7}\text{Mo}_6\text{S}_{7.4}\text{O}_{0.06}$ .Fig. 3. Cell voltage vs. lithium concentration  $x$  in NMSO for the first two cycles.

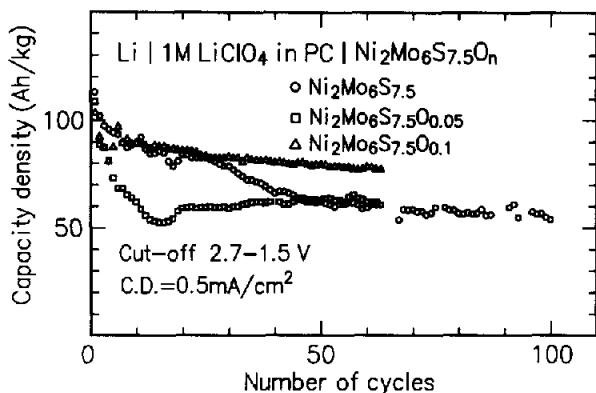


Fig. 4. Capacity density vs. cycle number for  $\text{Ni}_2\text{Mo}_6\text{S}_{7.5}\text{O}_n$ .

$\text{Ni}_2\text{Mo}_6\text{S}_{7.5}\text{O}_{0.1}$  for first two cycles in the voltage range of 1.5 to 2.7 V. The cell voltage of the second cycle increased compared with the first cycle, and this is due to the formation of second Chevrel phase which has higher discharge/charge voltages [5], while the capacity of the cell in the second cycle diminished. The cycling behavior for initial stage both on NMS and NMSO were very similar in each other, although these results were not shown.

The relationship between capacity density and cycles of  $\text{Ni}_2\text{Mo}_6\text{S}_{7.5}\text{O}_n$  ( $n = 0, 0.05, 0.1$ ) is shown in Fig. 4. The cathode properties of original NMS were almost the same as those of the previous study [7]. On the other hand, the NMSO cathode, especially at the composition  $\text{Ni}_2\text{Mo}_6\text{S}_{7.5}\text{O}_{0.1}$ , maintained higher capacity compared with oxygen free  $\text{Ni}_2\text{Mo}_6\text{S}_{7.5}$ . The capacity density of the  $\text{Ni}_2\text{Mo}_6\text{S}_{7.5}\text{O}_{0.1}$  should be 80 A h/kg and the theoretical energy density should be 152 W h/kg. Probably, the oxygen incorporated in the cluster structure would stabilize the structure itself and may contribute to improve the cyclic performance.

## Conclusions

The cathode properties of nickel Chevrel-phase sulfides for lithium secondary batteries were reexamined and recognized their promising cycling properties at room temperature.

Also, the cycling properties of nickel Chevrel-phase sulfides with partly-incorporated oxygen in the structure were tested as the cathode of rechargeable lithium batteries. The new cathode showed higher capacity than the original nickel Chevrel-phase sulfide even after the 60th cycle. The theoretical energy density of the new cathode was evaluated to be 152 W h/kg at the 50th cycle.

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