

## Thiospinels as cathode for lithium secondary battery

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### Abstract

The defect thiospinel  $\text{Cu}_x\text{M}_2\text{S}_4$  ( $\text{M}=\text{Ti}, \text{Cr}$ ) has been studied as a cathode material for the lithium secondary battery.  $\text{Cu}_{0.18}\text{Ti}_2\text{S}_4$  showed a good reversibility with smooth lithium intercalation and deintercalation. When it was cycled at the current density of  $1 \text{ mA cm}^{-2}$ , the discharge capacity of the first cycle was about  $170 \text{ mA h g}^{-1}$ , which corresponds to  $\text{Li}_{1.5}\text{Cu}_{0.18}\text{Ti}_2\text{S}_4$ . The defect  $\text{Li}_x\text{Cu}_{1-x}\text{Cr}_2\text{S}_4$  was prepared by the reaction of  $\text{CuCr}_2\text{S}_4$  and *n*-butyllithium. The reduced copper metal was deposited on the surface of the compound. This material did not show the reversible electrode reaction. The X-ray diffraction measurements indicated that the copper metal returned to the 8a sites of the spinel framework in the charge process. This copper atom blocks the lithium diffusion via 16c and 8a sites.

### Introduction

The high-rate rechargeability is an important factor of a cathode material for lithium secondary batteries. Some oxides and sulfides having a spinel structure have been investigated as a cathode for a Li secondary battery with high power density [1-3]. The spinel structure has three dimensional interstitial sites as pathways of Li diffusion. However, the diffusion rate of Li ions into the oxide spinels is generally small. The bottle neck size via 8a and 16c sites is too small for Li diffusion in an oxide framework, and A-site cations prevent the three-dimensional diffusion in the host lattice [4].

Recent papers have reported the Li diffusion in a large number of other type of spinel structures, for example, chloride spinels [5] and chalcogenide spinels [4]. In these compounds, the bottle neck size formed by the anions is larger than in the oxide spinels. If the immobile A-site cations can be removed from the lattice, these compounds can be expected to show the higher lithium ion mobility.

There are only a few studies about the electrochemical properties of the thiospinels as a cathode for a Li secondary battery, although a large number of varieties of spinel compounds are known. In this study, we tried to synthesize the defect thiospinel compounds which have the formula of  $\text{Cu}_x\text{M}_2\text{S}_4$  ( $\text{M}=\text{Ti}, \text{Cr}$ ) [4, 6]. Then, its possibility as a rechargeable cathode with high power density was discussed.

### Experimental

$\text{CuTi}_2\text{S}_4$  and  $\text{CuCr}_2\text{S}_4$  were prepared from the each element. Stoichiometric amount of the elements were mixed and sealed in an evacuated silica tube. In order to prepare

$\text{CuTi}_2\text{S}_4$ , the mixture was kept at 400 °C for 3 days, then heated again at 700 °C for 3 days. The extraction of the copper atom was carried out by oxidation at 60 °C for 3 weeks using  $\text{I}_2/\text{CH}_3\text{CN}$  solution. The copper and titanium ratio was determined by the atomic absorption method and the limiting composition was determined to be  $\text{Cu}_{0.18}\text{Ti}_2\text{S}_4$ . In the case of  $\text{CuCr}_2\text{S}_4$ , the silica tube was heated at 400 °C for 1 day, then heated again at 700 °C for 3 days. The products were ground once, then heated in vacuum at 700 °C for 3 days. The copper extraction from  $\text{CuCr}_2\text{S}_4$  by the oxidation with the  $\text{I}_2/\text{CH}_3\text{CN}$  did not succeed. Then, an ion exchange with Li was attempted by reaction with 1.6 M n-butyllithium in hexane at room temperature.

Charge/discharge tests were carried out by using a coin-type cell. 70 mg of the cathode material and 2 mg of polytetrafluoroethylene (PTFE) were mixed and pressed under 10 MPa pressure into a tablet with an 8 mm diameter. A Li sheet of 0.34 mm thickness was used as an anode. The electrolyte was a solution of 1 M  $\text{LiClO}_4$  dissolved in a mixture of propylene carbonate (PC) and dimethoxyethane (DME) solvent.

## Results and discussion

The  $\text{Cu}_x\text{Ti}_2\text{S}_4$  was obtained as a single phase for a composition range of  $0.18 < x < 1.0$  as shown in Fig. 1. The (220) diffraction peak indicating the existence of cations at the 8a sites of the spinel framework decreases with the oxidation and almost diminishes in  $\text{Cu}_{0.18}\text{Ti}_2\text{S}_4$ . This behavior clearly indicates that the copper atom is removed from the spinel lattice by chemical oxidation.

Figure 2 shows the discharge curve of  $\text{Cu}_{0.18}\text{Ti}_2\text{S}_4$  at various current densities and open-circuit voltage (OCV) curves for charge and discharge processes.  $\text{Cu}_{0.18}\text{Ti}_2\text{S}_4$  shows a stable voltage of about 2 V for a composition range of  $0 < x < 1.2$  in  $\text{Li}_x\text{Cu}_{0.18}\text{Ti}_2\text{S}_4$ . No significant degradation of discharge behavior was observed for the applied current densities below  $3 \text{ mA cm}^{-2}$ . The coulomb density at  $0.2 \text{ mA cm}^{-2}$  is  $177 \text{ mA h g}^{-1}$  based on a 1.0 V cutoff. The OCV curves show the typical S-shaped profile indicating

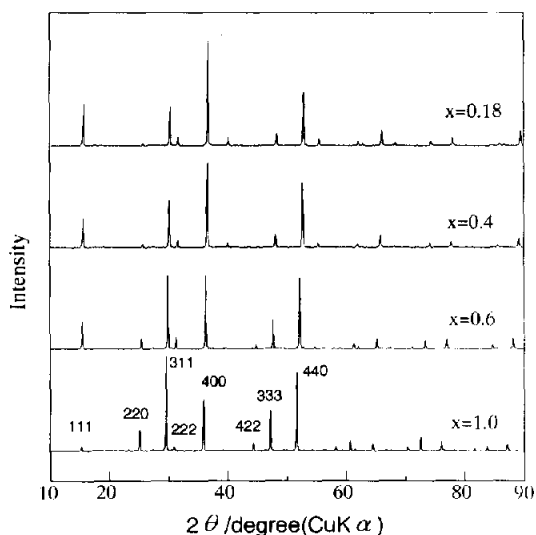


Fig. 1. XRD patterns of  $\text{Cu}_x\text{Ti}_2\text{S}_4$  at various oxidation states.

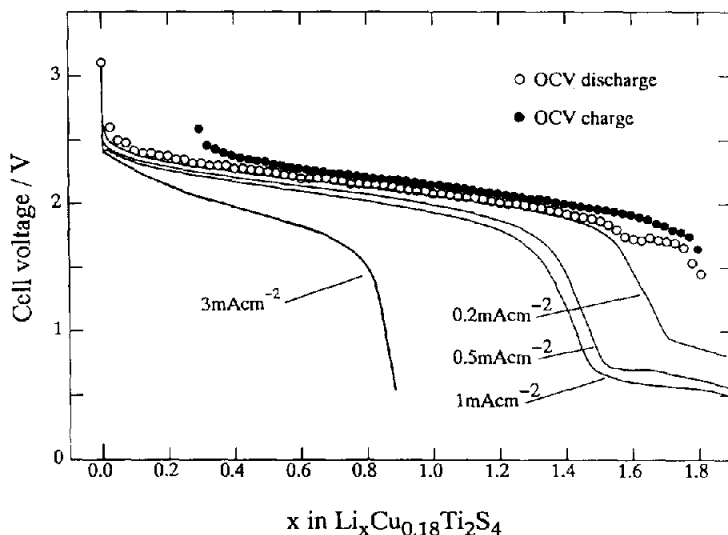


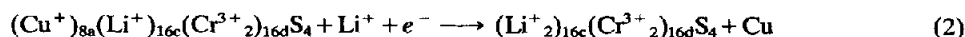
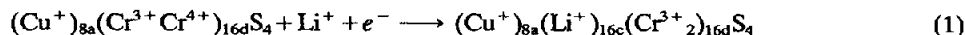
Fig. 2. Open-circuit voltage and discharge curves of the  $\text{Li}/\text{Cu}_{0.18}\text{Ti}_2\text{S}_4$  cells at various current densities.

the reaction of a single phase, that is, formation of a Li-thiospinel solid solution. The OCV curves of discharge and charge directions show almost the same profile over the whole range of  $x$ . This means that smooth Li insertion and extraction occur in both processes.

Figure 3 shows the variation of the lattice constant as a function of  $x$  in  $\text{Li}_x\text{Cu}_{0.18}\text{Ti}_2\text{S}_4$  for both the discharge and charge processes on cycling. The  $a$ -axis linearly increases with the discharge capacity, which results in a 7.8% expansion in volume of the unit cell at  $x = 1.8$ . At the charge side, the perfect recovery of the lattice constant is observed. This compound shows reversible lattice expansion and contraction on cycling.

Figure 4 shows cycling behaviors of the  $\text{Li}/\text{Li}_x\text{Cu}_{0.18}\text{Ti}_2\text{S}_4$  cell. The cycling test was carried out between 3.0 and 1.2 V at current densities of  $1 \text{ mA cm}^{-2}$ . The coulomb densities of the first cycle are about 170 and  $130 \text{ mA h g}^{-1}$  for the discharge and charge process, respectively, which corresponds to  $x = 1.5$  and 1.2 in  $\text{Li}_x\text{Cu}_{0.18}\text{Ti}_2\text{S}_4$ . The cycle efficiencies are 80% for the first cycle and almost 100% for the 5th cycle.

On the other hand, the defect  $\text{CuCr}_2\text{S}_4$  shows different behavior from  $\text{CuTi}_2\text{S}_4$ . The X-ray diffraction (XRD) patterns of  $\text{CuCr}_2\text{S}_4$  and its lithiated phase marked by the closed circles are shown in Fig. 5. Silicon powder was used as the internal standard material. As the reaction with *n*-butyllithium proceeds, the intensity of  $\text{CuCr}_2\text{S}_4$  decreases and the new peaks of a cubic phase with  $a = 10.00 \text{ \AA}$  increases. At the same time, the peaks of copper metal appear. The new cubic phase marked by closed circles is considered to be a lithiated spinel,  $\text{Li}_x\text{Cu}_{1-y}\text{Cr}_2\text{S}_4$ . The lattice constant is  $a = 10.00 \text{ \AA}$ , which is 1.8% larger than that of the starting material,  $\text{CuCr}_2\text{S}_4$ . These results indicate that the inserted Li induces the copper atom to be extracted from the host lattice, and the extracted copper metal deposits on the surface of the compounds. The reaction process can be described in an idealized form as follows:



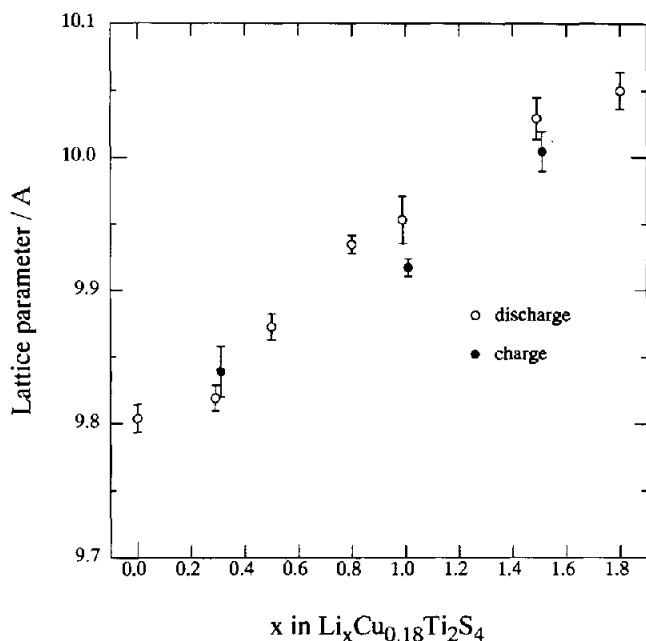


Fig. 3. The variation of the lattice parameter of the  $\text{Li}_x\text{Cu}_{0.18}\text{Ti}_2\text{S}_4$  on the first charge/discharge cycle.

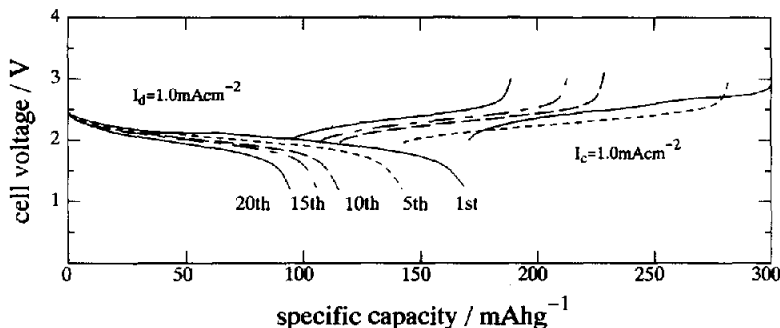


Fig. 4. The cycling profiles of the  $\text{Li}/\text{Cu}_{0.18}\text{Ti}_2\text{S}_4$  cells at the current density of  $1 \text{ mA cm}^{-2}$ .

The copper atom at the 8a site is extracted by the electrostatic repulsion with the Li atom at the 16c site. This behavior can be observed for other type of compounds [7, 8].

The electrochemical tests were started, at first, by charging this material. The charging behavior at a current density of  $0.2 \text{ mA cm}^{-2}$  is shown in Fig. 6. The initial voltage of  $\text{Li}_x\text{Cu}_{1-y}\text{Cr}_2\text{S}_4$  is about 2.8 V and the voltage sharply increases up to 4.0 V just after the charge process starts. Then the voltage drops again and shows a plateau at 2.6 V. The total voltage profile is similar to that of  $\text{Cu}_x\text{Ti}_2\text{S}_4$  except for the initial voltage overshoot. However, the following discharge profile is impossible to measure because the polarization becomes too large. In order to clarify the reason

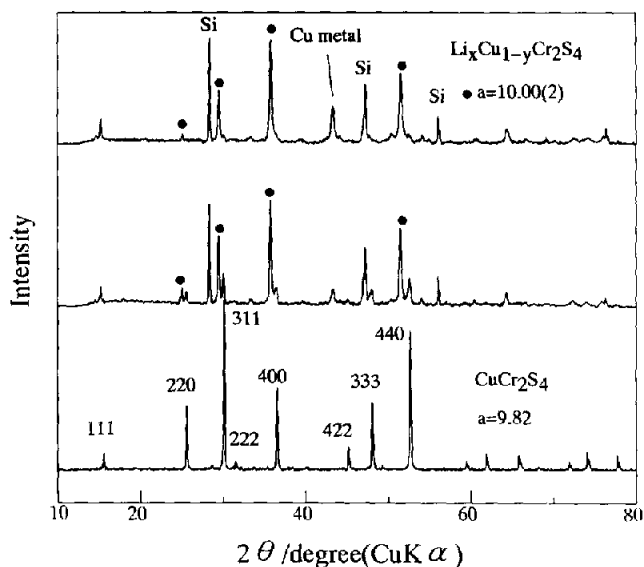


Fig. 5. The XRD patterns of reduced products by the reaction of  $\text{CuCr}_2\text{S}_4$  and n-butyllithium. The closed circles show a new phase appeared with the lithiation.

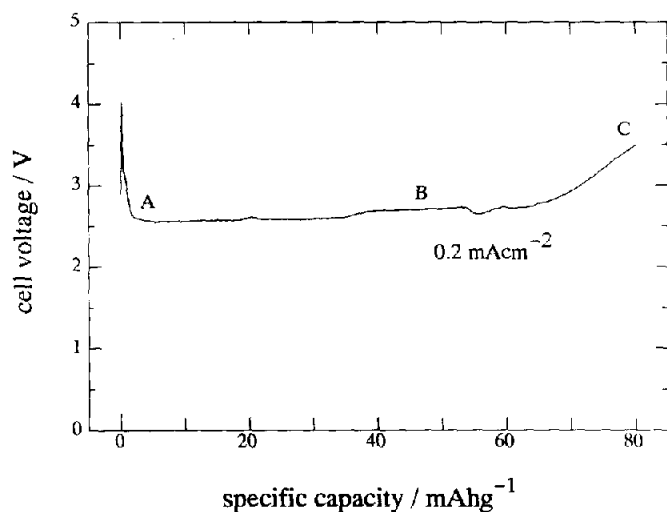


Fig. 6. The charge curve of the  $\text{Li}/\text{Li}_x\text{Cu}_{1-y}\text{Cr}_2\text{S}_4$  cell at the current density of  $0.2 \text{ mA cm}^{-2}$ .

for irreversibility of  $\text{Li}_x\text{Cu}_{1-y}\text{Cr}_2\text{S}_4$ , XRD measurements were carried out for samples charged at several stages, which are indicated as A, B, and C on the charge curve in Fig. 6.

Figure 7 shows the XRD patterns of the indicated A, B, and C stages on the charge curve. The starting material before charging shows a strong copper peak corresponding to copper metal deposited on the surface. The intensity decreases along the charge process and the peaks almost diminish at the C point of the charge curve

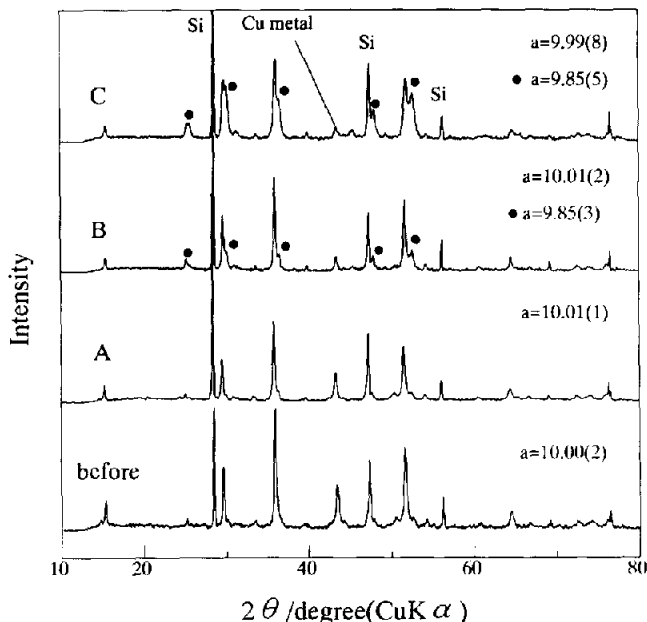


Fig. 7. The XRD patterns of  $\text{Li}_x\text{Cu}_{1-x}\text{Cr}_2\text{S}_4$  at several charged states. The closed circles show the spinel,  $\text{CuCr}_2\text{S}_4$ .

in Fig. 6. In addition, the new phase, marked by closed circles, appears, which is indexed as a thiospinel phase having a smaller lattice constant ( $a = 9.85 \text{ \AA}$ ). The XRD pattern of this phase is similar to that of  $\text{CuCr}_2\text{S}_4$  ( $a = 9.82 \text{ \AA}$ ) in Fig. 5. It is worthy to note that the (220) peak of the new phase at around  $25^\circ(2\theta)$  indicates the existence of a cation on 8a tetrahedral sites. The light Li atom can give only small contribution to the XRD intensity, therefore, the most probable explanation is that the copper atom occupies the 8a sites. Thus, we can conclude that the copper metal on the surface returns to the 8a sites with the extraction of Li ion.

## Conclusion

The defect thiospinel,  $\text{Cu}_{0.18}\text{Ti}_2\text{S}_4$  is proved to be a candidate for cathode material, which can be cycled at the high current density. However, it is important to remove the copper atom in advance. The residual copper in the lattice prevents the smooth diffusion of Li ions and, therefore, the smooth charge/discharge reaction.

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