

DEFECT THIOSPINELS: A NEW CLASS OF REVERSIBLE CATHODE MATERIAL

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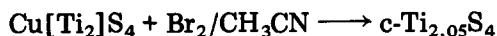
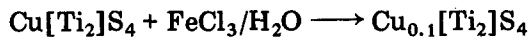
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Summary

The defect thiospinel $\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ was prepared by low-temperature oxidative extraction of copper from $\text{Cu}[\text{Ti}_2]\text{S}_4$. Up to two equivalents of lithium can be inserted into $\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ reversibly with fast electrochemical kinetics at room temperature; the defect thiospinel is, therefore, a highly promising alternative to layered TiS_2 as a cathode material for lithium secondary batteries. Samples of $\text{Cu}_{1-x}[\text{Ti}_2]\text{S}_4$ ($0 \leq x \leq 0.93$) and $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ ($0 < x < 2$) were prepared and characterised by ^{65}Cu and ^7Li solid-state NMR, neutron powder diffraction, and electrochemical measurements. $\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ is a semimetal with the residual copper located on the normal spinel A-cation sites. The lithium in $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ is located only in the 16c octahedral sites of the spinel framework at all lithium compositions. The open-circuit voltage of $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ versus lithium metal is nearly identical to that of layered Li_xTiS_2 over the whole lithium-composition range. The chemical diffusion constant of lithium in $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ ($0.5 \leq x \leq 1.5$) was found to be $1 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, which is comparable with that in layered Li_xTiS_2 .

Introduction

Two recent papers by Schollhorn & Payer [1] and by Sinha & Murphy [2] have reported that copper can be oxidatively extracted from the normal thiospinel $\text{Cu}[\text{Ti}_2]\text{S}_4$ with mild oxidising agents at room temperature to give defect thiospinels of approximate composition $\text{Cu}_{0.1}[\text{Ti}_2]\text{S}_4$. The presence of a small excess of titanium in the starting material enabled all of the copper to be extracted to give the novel, cubic titanium sulfide $\text{c-Ti}_{2.05}\text{S}_4$ [2]:



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The authors further reported that up to two equivalents of lithium could be inserted into the defect thiospinels $\text{Cu}_{0.1}[\text{Ti}_2]\text{S}_4$ and $\text{c-Ti}_{2.05}\text{S}_4$ reversibly at room temperature, that the open-circuit voltage for electrochemical lithium insertion was comparable to that of layered Li_xTiS_2 over the whole lithium-composition range, and that the lithium-ion mobility in the lithiated defect thiospinels appeared to be high. The defect thiospinels are thus highly promising cathode materials for lithium secondary batteries; for this purpose they would offer the following important advantages over layered TiS_2 : three-dimensional electronic and ionic conductivity, an isotropic lattice expansion on lithium insertion, no tendency to intercalate water or solvent molecules from the electrolyte, and easy control of titanium stoichiometry.

The objectives of the study described below were as follows:

— to study the effect of copper extraction on the structure and bonding of the $[\text{Ti}_2]\text{S}_4$ framework in the defect thiospinels $\text{Cu}_{1-x}[\text{Ti}_2]\text{S}_4$ ($0 \leq x \leq 0.93$) and to determine the nature of the residual copper at the limiting composition $\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$;

— to locate the inserted lithium in the lithiated defect thiospinels $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ ($0 < x < 2$) by neutron powder diffraction and ^7Li solid-state NMR;

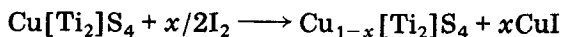
— to measure the open-circuit voltage *versus* lithium metal and the lithium-ion chemical diffusion constant in $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ ($0 < x < 2$) at room temperature as a function of lithium composition.

A more detailed account of experimental methods and a fuller discussion of the results described below will be given in separate publications [3 - 6].

Chemical synthesis

The metallic, normal thiospinel $\text{Cu}[\text{Ti}_2]\text{S}_4$ was prepared by direct synthesis from the elements at 350 - 750 °C. Repeated grinding and sintering under high vacuum at 750 °C ensured a product of high crystallinity and chemical homogeneity.

Oxidative extraction of copper from $\text{Cu}[\text{Ti}_2]\text{S}_4$ was undertaken by vigorous stirring with a controlled excess of 0.2 M I_2 /acetonitrile solutions for 7 - 21 days at 45 °C:



Iodine is preferable to the FeCl_3 or Br_2 solutions used previously [1, 2] because it is specific for the copper extraction reaction and shows no tendency to oxidise sulfide ions. The CuI is readily removed, since it is soluble in acetonitrile to the extent of 35 g l^{-1} at 35 °C. The limiting composition for oxidative copper extraction was $\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$; no more copper could be extracted, even at elevated temperature or with stronger oxidising agents such as bromine.

Chemical lithiation of $\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ was carried out by vigorous stirring with controlled quantities of 0.1 M *n*-butyllithium in hexane at room temperature under a reduced pressure of dry nitrogen. The product was isolated with standard Schlenk techniques, pressed into pellets, and annealed under high vacuum ($p < 10^{-4}$ Torr) at 250 °C for 24 h to ensure chemical homogeneity. The limiting composition for chemical lithiation was $\text{Li}_{1.93}\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$.

The defect thiospinels $\text{Cu}_{1-x}[\text{Ti}_2]\text{S}_4$ ($0 \leq x \leq 0.93$) were not appreciably air-sensitive, but all manipulations of these materials were carried out with the total exclusion of air and moisture as a precaution against surface hydrolysis. The lithiated materials $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ ($0 < x < 2$) hydrolyse slowly in air.

Results and discussion

(i) The defect thiospinels $\text{Cu}_{1-x}[\text{Ti}_2]\text{S}_4$ ($0 \leq x \leq 0.93$)

The X-ray powder-diffraction patterns of the defect thiospinels $\text{Cu}_{1-x}[\text{Ti}_2]\text{S}_4$ ($0 \leq x < 0.93$) show that the cubic lattice parameter of these materials decreases linearly by up to 3% as copper is extracted (Fig. 1). Neutron powder diffraction of the limiting phase $\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ showed that the $[\text{Ti}_2]\text{S}_4$ framework is otherwise unaffected by the copper extraction and enabled the residual copper to be located on the normal A-cation sites (the 8a tetrahedral sites) of the spinel framework; we can conclude that there is no structural obstacle to extraction of this copper.

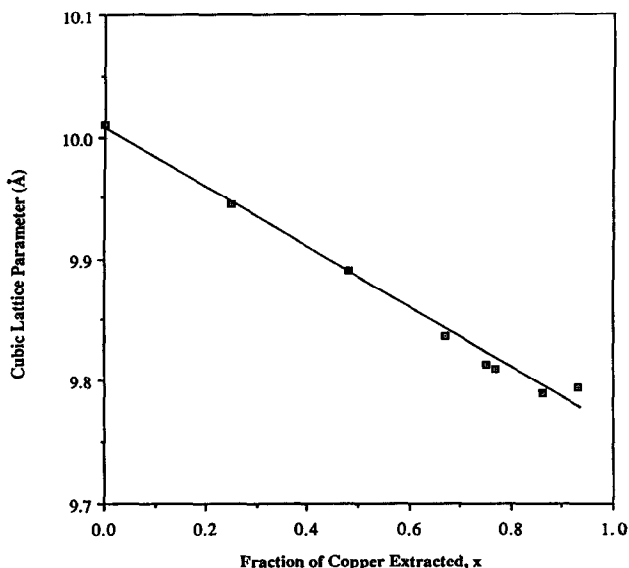


Fig. 1. Cubic lattice parameter of the defect thiospinels $\text{Cu}_{1-x}[\text{Ti}_2]\text{S}_4$ ($0 \leq x < 0.93$).

Static ^{65}Cu NMR spectra (at 56.79 MHz) were obtained for the phases $\text{Cu}_{1-x}[\text{Ti}_2]\text{S}_4$ with $x = 0, 0.25, 0.75$ and 0.93 . In each case, a single ^{65}Cu resonance with a large Knight shift ($\delta > +2000$ ppm) was observed; the paramagnetic shifts were comparable to that of ^{65}Cu in metallic copper; these observations imply that all of the $\text{Cu}_{1-x}[\text{Ti}_2]\text{S}_4$ defect phases are metallic or semimetallic and that the conduction electrons in these materials have substantial Cu-4s character.

The magnetic susceptibilities of the $\text{Cu}_{1-x}[\text{Ti}_2]\text{S}_4$ defect phases with $x = 0, 0.25, 0.75$ and 0.93 were measured in the temperature range 77 - 293 K. The copper-deficient phases all showed weak, temperature-independent paramagnetism (Pauli paramagnetism) with molar susceptibilities corrected for atomic diamagnetism in the range $200 - 300 \times 10^{-6} \text{ emu mol}^{-1}$. The parent thiospinel $\text{Cu}[\text{Ti}_2]\text{S}_4$ exhibited stronger; temperature-dependent paramagnetism ($520 \times 10^{-6} \text{ emu mol}^{-1}$ at 293 K). This behaviour is probably due to the presence of a paramagnetic impurity in the $\text{Cu}[\text{Ti}_2]\text{S}_4$ that is dissolved away by the iodine/acetonitrile solutions used to extract copper. The measured magnetic susceptibility of $\text{Cu}[\text{Ti}_2]\text{S}_4$ was very similar to that reported previously by Le Nagard *et al.* [7].

The structural evidence and physical measurements presented above lead us to conclude that the defect thiospinel at the limiting composition $\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ is a semimetal because of overlap between the predominantly S-3p valence band and the predominantly Ti-3d and Cu-4s conduction band. The semimetallic nature of $\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ is not unexpected, since layered TiS_2 is known to be a semiconductor with a bandgap of only 0.3 eV [8, 9]. Further oxidative copper extraction from $\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ is impossible because the electrons at the Fermi level have sufficient S-3p character for oxidation of the sulfide lattice to be the preferred oxidation reaction.

(ii) Structural and ^7Li NMR study of the lithiated defect thiospinels

$\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ ($0 < x < 2$)

X-ray powder diffraction of the lithiated defect thiospinels $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ ($0 < x < 2$) showed that the thiospinel cubic lattice parameter increases linearly with x by up to 2.6% on lithiation. Samples of $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ with $x = 0.93$ and 1.93 were submitted for neutron powder diffraction; Rietveld refinement of the diffraction profiles showed that the inserted lithium occupies only the 16c octahedral sites of the thiospinel framework at both compositions.

Static and MAS ^7Li NMR spectra at 77.73 MHz of $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ with $x = 0.35, 0.73, 0.90, 1.73$ and 1.93 were measured at room temperature. All of the spectra show lithium in a single chemical environment with a small chemical shift relative to lithium acetate dihydrate; the paramagnetic component of the chemical shift, which is presumably a Knight shift due to conduction-electron density at the lithium nuclei, increases linearly with x . The overall chemical shift ranges from -4.45 ppm at $x = 0.35$ to $+12$ ppm at $x = 1.93$. By comparison, the chemical shift in metallic lithium is $+250$ ppm. The ^7Li NMR spectra of $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ also show the onset of quadrupolar

line broadening (~ 20 kHz) and a Knight-shift anisotropy for $x \geq 0.90$; these effects are presumably due to interactions between inserted lithium ions on neighbouring edge-sharing 16c sites as the lithium content increases. Lithium-ion hopping, which has a frequency of about 1 MHz in these materials at room temperature, must play a part in averaging out lithium-lithium interactions at lower lithium contents.

(iii) *Electrochemistry of the lithiated defect thiospinels $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ ($0 < x < 2$)*

Figure 2 shows the discharge open-circuit voltage (OCV) of $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ versus lithium metal as a function of lithium composition, x . In agreement with Sinha and Murphy [2], the OCV is roughly comparable with that of layered Li_xTiS_2 over the whole lithium composition range, but it does not exhibit the plateau at $x < 0.3$ of the layered phase that is due to solvent intercalation [10]. The absence of any discontinuity in the OCV at the normal spinel composition $\text{Li}_{0.93}\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ is consistent with the neutron-diffraction data, presented above, which suggest that the inserted lithium occupies only the 16c octahedral sites of the spinel framework at all lithium compositions.

The chemical diffusion coefficient (D) of the lithium ions in $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ ($0.1 \leq x \leq 1.85$) was measured as a function of lithium composition by an a.c. impedance method [4, 11, 12]; the results are given in Table 1. D in $\text{Li}_{1.0}\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ was also measured by a galvanostatic pulse technique [4, 13]. Both methods gave $D = 1 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ over most of the lithium composition range ($0.5 \leq x \leq 1.5$), but the a.c. impedance experiment

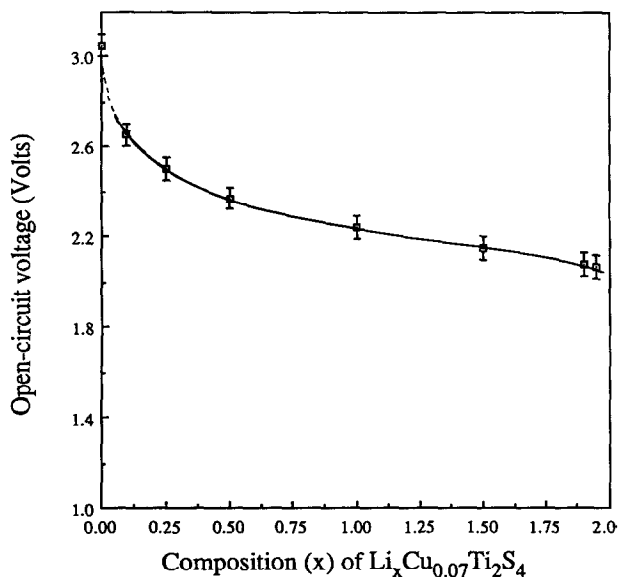


Fig. 2. Open circuit voltage (OCV) of $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ ($0 < x < 2$) vs. metallic lithium.

TABLE 1

Transport properties of lithium in $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ determined by a.c. impedance measurements

x	D ($\text{cm}^2 \text{s}^{-1}$)	D_{Li} ($\text{cm}^2 \text{s}^{-1}$)	σ_{Li} ($\Omega^{-1} \text{cm}^{-1}$)	μ_{Li} ($\text{cm}^2 \text{s}^{-1} \text{V}^{-1} \text{mol}^{-1}$)
0.1	5×10^{-11}	1×10^{-11}	7×10^{-8}	6×10^{-15}
0.5	1×10^{-9}	2×10^{-10}	4×10^{-6}	6×10^{-14}
1.0	5×10^{-10}	6×10^{-11}	3×10^{-6}	2×10^{-14}
1.5	2×10^{-9}	2×10^{-10}	1×10^{-5}	5×10^{-14}
1.85	2×10^{-10}	7×10^{-12}	4×10^{-7}	2×10^{-15}

D is the lithium-ion chemical diffusion coefficient; D_{Li} is the lithium-ion self-diffusion coefficient.

σ_{Li} is the lithium-ion partial conductivity; μ_{Li} is the lithium-ion mobility.

suggested that D is an order of magnitude lower at the extreme compositions $x = 0.1$ and $x = 1.85$. The measured values of D correspond to an average partial lithium-ion conductivity $\sigma_{\text{Li}} = 6 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$. The lithium-ion chemical diffusion coefficient in $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ is similar to that in layered Li_xTiS_2 ; an accurate comparison is difficult because published values of D in Li_xTiS_2 range over two orders of magnitude [14]. The partial lithium-ion conductivity in $\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ is about one order of magnitude lower than that in the defect chloride spinel $\text{Li}_{0.8}[\text{Li}_{0.8}\text{Mg}_{1.2}]\text{Cl}_4$ ($\sigma_{\text{Li}} = 5 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$), which has been studied as a possible lithium solid electrolyte [15]. The difference between the thiospinel and the chloride spinel can be accounted for by the larger bottleneck size and the lower electrostatic potential energy barrier for lithium-ion hopping in the chloride.

Finally, we note that the a.c. impedance spectrum of an $\text{Li}|\text{Li}^+|\text{Li}_x\text{Cu}_{0.07}[\text{Ti}_2]\text{S}_4$ cell can be modeled accurately by a Randles equivalent circuit [4]; this implies that the cell is a straightforward electrochemical system with a homogeneous, isotropic cathode and with no surface layer formation. The ohmic resistance and the charge transfer resistance of the cell are low. We can conclude that the cell polarisation under normal discharge conditions will be determined primarily by the cell morphology and the rate of lithium-ion diffusion in the cathode.

Acknowledgements

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