Chalcogen rearrangement in the Chevrel compound $InMo_6Se_zS_{8-z}$ at 500°C

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We prepared two sets of lithium insertion compounds of $Li_xMo_6Se_zS_{8-z}$ with $z=4$, 5, 6, 7, and 8, by removing copper chemically from $Cu_{2.5}Mo_6Se_zS_{8-z}$, and then (1) adding lithium in electrochemical cells, or (2) preparing $InMo_6Se_zS_{8-z}$ by annealing indium and $Mo_6Se_zS_{8-z}$ powders at 500 °C, and then replacing the indium with lithium in electrochemical cells. The variation of voltage of these electrochemical cells with x is different for the two sets, suggesting that the treatment of the second set at 500 °C has modified the distribution of sulfur and selenium around the Li sites. We confirmed this change with single-crystal x-ray diffraction on $Cu_{2.5}Mo_6Se_4S_4$, $Cu_{2.0}Mo_6Se_4S_4$, $Mo_6Se_4S_4$, and $InMo_6Se_4S_4$.

I. INTRODUCTION

For Li content x in the range $0 < x < 1$ in the Chevrel compounds $Li_xMo_6S_8$ (Ref. 1) and $Li_xMo_6Se_8$,[2,3] lithium atoms occupy sites on the $\bar{3}$ axis and have a site energy (the energy to remove a lithium atom from lithium metal and place it into these sites) of -2.41 and -2.07 eV, respectively. These lithium sites are in a cage of eight chalcogens, each chalcogen from a different Mo_6S_8 or Mo_6Se_8 cluster.[4,5] In the mixed sulfur-selenium compounds $Mo_6Se_zS_{8-z}$, the distribution of chalcogens in this cage creates a range of possible lithium site energies between -2.41 and -2.07 eV, depending on how many of the chalcogens are S or Se. The two chalcogens on the $\bar{3}$ axis (in the Wyckoff special position $2c$) have the greatest influence on the lithium site energy, because they are about 1 Å closer to the lithium atoms than are the other six chalcogens (in the Wyckoff general positions $6f$).[6] Thus, as lithium atoms are added to $Mo_6Se_zS_{8-z}$, they fill sites according to how many S atoms are in the special positions, filling sites coordinated by two sulfurs first, sites coordinated by one sulfur and one selenium next, and sites coordinated by two seleniums last.

In an earlier study of $Mo_6Se_zS_{8-z}$ using electrochemical methods,[6] we measured the energy and concentration of these three types of lithium sites. We found that each of the two chalcogens on the $\bar{3}$ axis is about 10 times more important in determining the lithium site energy than any of the next six nearest chalcogens. In addition, we found an enrichment of selenium in the special positions on the $\bar{3}$ axis; that is, we found more selenium in the special positions than would be expected if sulfur and selenium were randomly distributed over the special and general positions.

Recently, Cava found[7] that when indium is inserted into $Mo_6Se_zSe_{8-z}$ at 500 °C, the resulting compounds have an enrichment of sulfur, not selenium, in the special positions on the $\bar{3}$ axis. This difference in chalcogen occupancies is unexpected, since both series of $Mo_6Se_zSe_{8-z}$ were prepared similarly, by chemical removal of copper[8,9] from $Cu_{2.5}Mo_6Se_zS_{8-z}$ (Ref. 6) or

$Cu_{2.0}Mo_6Se_zSe_{8-z}$,[10,11] before lithium was added at room temperature or indium at 500 °C. To resolve this apparent discrepancy in chalcogen occupancies, we added indium at 500 °C to our $Mo_6Se_zSe_{8-z}$ samples and, as before, did single-crystal x-ray diffraction and electrochemical measurements. In this paper we present the results of this work and show that, at 500 °C in the presence of indium, the chalcogen distribution changes, and sulfur atoms replace selenium atoms in the positions on the $\bar{3}$ axis.

II. SAMPLE PREPARATION AND STRUCTURE

We prepared our host series from $Cu_{2.5}Mo_6Se_zS_{8-z}$, whereas Cava started from $Cu_{2.0}Mo_6Se_zS_{8-z}$, and so we first checked that the chalcogen occupancies are insensitive to this small difference in copper in the starting material. We prepared (as in Ref. 6) a crystalline powder of $Cu_2Mo_6Se_4S_4$, from which we selected a crystal for x-ray diffraction. This crystal belonged to the rhombohedral space group $R\bar{3}$ (C_{3i}^2), as determined from the refinement of about 500 measured reflections from graphite-monochromated Mo $K\alpha$ x rays up to $2\theta=60°$. All other experimental details and computations were as in Ref. 6. Table I lists interatomic distances and other structural parameters for $Cu_{2.5}Mo_6Se_4S_4$ and $Cu_2Mo_6Se_4S_4$, and confirms that these two compounds are similar, especially in the interatomic distances between the chalcogen atoms and interstitial sites, which lithium atoms would occupy were they present.

The chalcogen occupancies of these two host compounds, summarized in Table II, are almost identical, and both hosts have an enrichment of selenium over sulfur in the special positions. The occupancies in Table II were determined as follows: The chalcogen positions were first assumed to contain only Se with a fractional occupancy; then the positional and thermal parameters were fixed to the refined values, and the occupancies of the chalcogen positions by S or Se were refined, constrained to full occupancy of the eight available positions. The values of B_{iso}, the mean of the principal axes of the thermal ellipsoid, were calculated from the anisotropic thermal mo-

TABLE I. Structural parameters obtained from single-crystal x-ray diffraction for $Cu_{2.5}Mo_6Se_4S_4$, $Cu_{2.0}Mo_6Se_4S_4$, $Mo_6Se_4S_4$, and $InMo_6Se_4S_4$. The interatomic distances are accurate to the last digit quoted. Se indicates positions containing Se or S with Se(1) corresponding to an X_b position (six Wyckoff general positions off $\bar{3}$ axis) and Se(2) to an X_a position (two Wyckoff special positions on $\bar{3}$ axis). The copper or indium sites, labeled Cu(1) and Cu(In)(2), are, respectively, one of six outer or six inner interstitial sites. The densities (ρ) are calculated using the chemical formulas shown.

	$Cu_{2.5}Mo_6Se_4S_4$[a]	$Cu_{2.0}Mo_6Se_4S_4$	$Mo_6Se_4S_4$[a]	$InMo_6Se_4S_4$
Mo-Mo (Å)	2.68/2.72/3.39	2.69/2.74/3.35	2.71/2.85/3.15	2.69/2.37/3.31
Mo-Se (Å)	2.48–2.57	2.47–2.57	2.48–2.55	2.49–2.57
shortest Se-Se (Å)	3.47	3.46	3.30	3.41
Cu(1)-Se(1) (Å)	2.51/2.34/2.29	2.36/2.39/2.42		
Cu(1)-Se(2) (Å)	2.34	2.28		
Cu(In)(2)-Se(1) (Å)	2.24/2.33	2.26/2.29		2.54/2.63
Cu(In)(2)-Se(2) (Å)	2.52/2.43	2.43/2.53		2.41/2.46
Se(1)-Li site (Å)	3.32	3.30	3.15	3.19
Se(2)-Li site (Å)	2.05	2.07	2.27	2.31
crystal size (mm)	0.1×0.1×0.1		0.07×0.07×0.07	0.1×0.1×0.1
a_R (Å)	6.645(2)	6.632(2)	6.521(2)	6.606(3)
α_R (deg)	95.16(2)	94.78(2)	91.92(2)	93.22(2)
ρ (g cm^{-3})	6.758	6.602	6.117	6.568
residual R (%)	3.0	5.79	5.86	4.73
residual R_w (%)	2.4	6.02	5.23	5.57
observed reflections for R_w ($>2\sigma$)	465	490	452	472

[a]From Ref. 6.

tion refined for all atoms.

Having verified that our starting materials $Mo_6Se_zS_{8-z}$ were enriched in selenium in the chalcogen positions on the $\bar{3}$ axis, we then prepared $InMo_6Se_zS_{8-z}$ samples with $z=4$, 5, 6, 7, and 8. We added enough indium powder (Aldrich 99.98%) to $Mo_6Se_zS_{8-z}$ powder to make $InMo_6Se_zS_{8-z}$ and annealed these mixtures at 500 °C for 1 week. We further annealed the sample of $InMo_6Se_7S$

TABLE II. Site occupancy, atom positions, and thermal parameters obtained from single-crystal x-ray diffraction. The chemical formulas in brackets are calculated from the refinement. The chalcogen positions and copper sites are labeled as in Table I. The standard deviation for the last printed digit is shown in brackets. Data in (a) and (c) are from Ref. 6.

	Site	Occupancy	x	y	z	B_{iso} (Å^2)
		(a) $Cu_{2.5}Mo_6Se_4S_4$ ($Cu_{2.6}Mo_6Se_{3.4}S_{4.6}$)				
Mo	$6f$	1	0.2282(1)	0.4080(1)	0.5424(1)	0.62(5)
Se(1)/S(1)	$6f$	0.35(2)/0.65	0.3755(3)	0.1288(3)	0.7239(4)	1.0(1)
Se(2)/S(2)	$2c$	0.63(2)/0.37	0.1970(2)	0.1970	0.1970	0.9(1)
Cu(1)	$6f$	0.20(2)	0.6421(1)	0.0479(1)	−0.0126(1)	3.5(3)
Cu(2)	$6f$	0.23(2)	0.0986(1)	0.8338(1)	0.0521(1)	4.6(4)
		(b) $Cu_{2.0}Mo_6Se_4S_4$ ($Cu_{2.1}Mo_6Se_{3.5}S_{4.5}$)				
Mo	$6f$	1	0.2257(2)	0.4077(2)	0.5427(2)	0.70(5)
Se(1)/S(1)	$6f$	0.36(2)/0.64	0.3764(4)	0.1309(4)	0.7277(5)	1.0(1)
Se(2)/S(2)	$2c$	0.68(2)/0.32	0.1972(4)	0.1972	0.1972	1.1(1)
Cu(1)	$6f$	0.13(2)	0.630(4)	0.036(4)	−0.028(4)	3.5
Cu(2)	$6f$	0.23(2)	0.093(3)	0.833(4)	0.055(3)	4.6
		(c) $Mo_6Se_4S_4$ ($Mo_6Se_{3.6}Se_{4.4}$)				
Mo	$6f$	1	0.2162(3)	0.4073(3)	0.5485(3)	0.52(6)
Se(1)/S(1)	$6f$	0.37(4)/0.63	0.3806(5)	0.1284(5)	0.7430(4)	0.9(1)
Se(2)/S(2)	$2c$	0.70(4)/0.30	0.2084(4)	0.2084	0.2084	1.0(1)
		(d) $InMo_6Se_4S_4$ ($InMo_6Se_{3.5}S_{4.5}$)				
Mo	$6f$	1	0.2262(2)	0.4119(2)	0.5491(2)	0.90(4)
Se(1)/S(1)	$6f$	0.45(2)/0.54	0.3722(3)	0.1276(3)	0.7362(3)	1.2(1)
Se(2)/S(2)	$2c$	0.42(2)/0.57	0.2142(4)	0.2142	0.2142	1.6(1)
In(2)	$6f$	0.167	0.933(2)	0.088(6)	−0.028	7(2)

TABLE III. Rhombohedral lattice parameters for InMo$_6$Se$_z$S$_{8-z}$.

z	Cell edge (Å) (±0.001)	Cell angle (deg) (±0.01)	Cell volume (Å^3) (±0.1)
4	6.628	93.12	289.8
5	6.674	93.26	295.8
6	6.695	93.04	298.8
7	6.748	93.03	306.0
7	6.751	89.65	307.6
8	6.784	89.15	312.0

for an additional 2 weeks at 520 °C. The final products were single phase as determined by x-ray powder diffraction using a Stoe Bragg-Brentano powder diffractometer and Ni-filtered Cu $K\alpha$ radiation.

The rhombohedral lattice parameters for InMo$_6$Se$_z$S$_{8-z}$, $z=4$, 5, 6, 7, and 8, were determined by least-squares refinement of the position of at least 20 Bragg peaks. Our results are tabulated in Table III and are shown in Fig. 1 (solid circles) along with those of Tarascon et al.[12] (open circles). For InMo$_6$Se$_7$S, we measured two different sets of lattice parameters and have in-
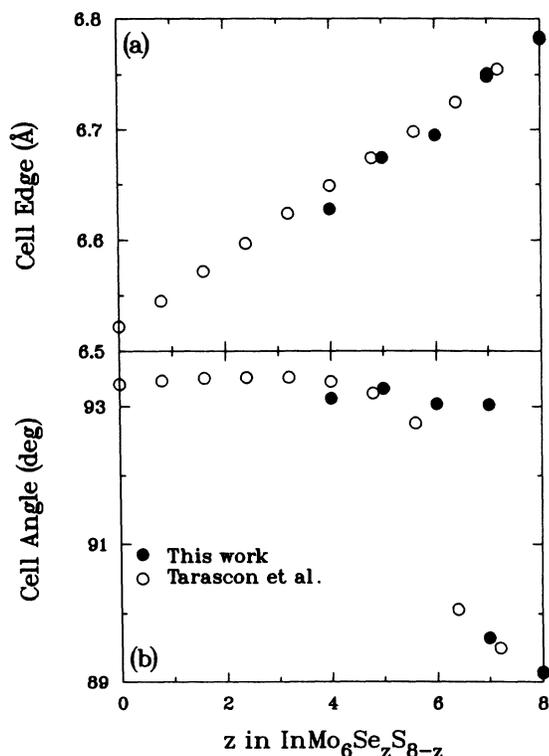

FIG. 1. Rhombohedral unit-cell lattice parameters vs selenium content z in InMo$_6$Se$_z$S$_{8-z}$. (a) Length of rhombohedral unit-cell edge; (b) rhombohedral unit-cell angle. Solid circles are for this work, and open circles are from Tarascon et al. (Ref. 12).

cluded both in Fig. 1. After an anneal for 1 week at 500 °C, the rhombohedral angle α_R was high, at about 93°. After a further anneal at 520 °C for 2 more weeks, α_R decreased to 89.6°, whereas the rhombohedral cell edge a_R changed negligibly. The final cell parameters of this second sample agree with those observed by Tarascon et al.[12]

The changes in α_R in InMo$_6$Se$_7$S with annealing suggests a slow rearrangement of atoms near 500 °C. Yvon[4] has discussed the correlation between α_R and the location of the guest atoms in the host. When α_R is greater than 90°, the guest atoms are located in a ring of six small sites located off the $\bar{3}$ axis; when α_R is roughly 90° or less, the guest atoms are located in a single, larger site on the $\bar{3}$ axis. The difference in α_R in the two InMo$_6$Se$_7$S samples implies that the indium's position changes with annealing; these changes are probably caused by the changes (discussed below) of the amounts of selenium and sulfur in the special 2c positions.

After making InMo$_6$Se$_z$S$_{8-z}$ for $z=4$, 5, 6, 7, and 8, we selected a single crystal of InMo$_6$Se$_4$S$_4$ and measured the x-ray diffraction data. The structural results and interatomic distances are listed in Table I along with our previous results[6] on a single crystal of Mo$_6$Se$_4$S$_4$. The main structural difference in these two crystals is the rhombohedral angle α_R; α_R is smaller in Mo$_6$Se$_4$S$_4$ (91.92°) than in InMo$_6$Se$_4$S$_4$ (93.22°). According to the discussion of Yvon,[4] the larger value of α_R in InMo$_6$Se$_4$S$_4$ suggests that the indium atoms are located in a delocalized ring around the $\bar{3}$ axis, rather than at the origin of the unit cell. This interpretation is supported by the large value of B_{iso} for indium in Table II.

The occupancies of the chalcogen positions in InMo$_6$Se$_4$S$_4$ are given in Table II with, for comparison, the data on Mo$_6$Se$_4$S$_4$ from Ref. 6. In the single crystal of Mo$_6$Se$_4$S$_4$, the ratio of Se:S in the chalcogen positions on the $\bar{3}$ axis is 0.70:0.30. In InMo$_6$Se$_4$S$_4$ the ratio of Se:S in the same position has decreased to 0.42:057. This change, we emphasize, has occurred after indium entered the host as the sample was annealed for 1 week at only 500 °C.

III. MEASUREMENTS ON ELECTROCHEMICAL CELLS

Electrochemical cells were constructed using powders of InMo$_6$Se$_z$S$_{8-z}$ on Ni foil as one electrode and Li metal foil as the other, as described by Dahn and Haering.[13] The electrodes were separated by porous polypropylene film (Celgard 3501) soaked in 1M LiAsF$_6$ (USS Agri-Chemicals) in distilled propylene carbonate. The voltage V was monitored as a function of time as the cells were discharged and charged at a constant current at 28 °C. The currents were chosen such that $\Delta x=1$ in 10–40 h (which we call a 10–40-h rate).

Figure 2 shows the voltage versus x of a Li/Li$_x$InMo$_6$Se$_7$S cell during its first discharge to 1.2 V and subsequent cycles between 2.6 and 1.2 V. This cell was not discharged below 1.2 V, where there is an additional voltage plateau associated with the irreversible decomposition of the host material into Li$_2$S, Li$_2$Se, and
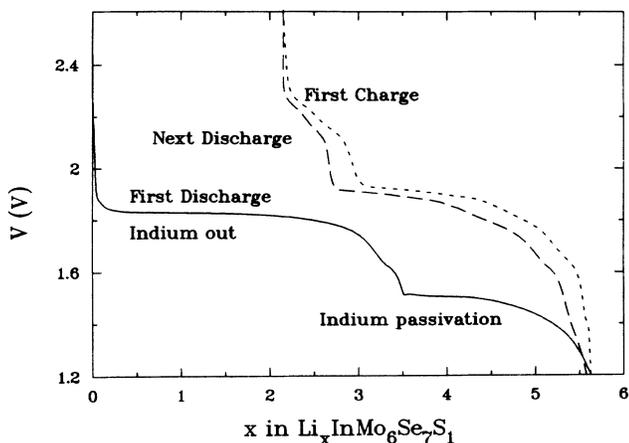
FIG. 2. Voltage V vs lithium content x for a Li/Li$_x$InMo$_6$Se$_7$S cell, measured at 1 0-h rate and 28 °C. Indium is forced out of the host at 1.8 V, and a passivation reaction at 1.5 V prevents indium from returning to the host when the cell is charged. The InMo$_6$Se$_7$S used was annealed 1 week at 500 °C and 2 weeks at 520 °C.

the solvent propylene carbonate or the electrolyte LiAsF$_6$, that somehow prevents indium from returning to the host. The Li content of the host phases returns to zero at the top of the charge; the apparent Li still present at the top of the first charge represents the amount of charge consumed in the irreversible reaction of the displaced indium.

To study electrochemically the chalcogen distribution in the host Mo$_6$Se$_z$S$_{8-z}$ after an anneal in the presence of indium, we took advantage of the indium passivation reaction to remove the indium from our InMo$_6$Se$_z$S$_{8-z}$ samples. After discharging the cells to 1.2 V to remove and passivate the indium, we obtained the $V(x)$ curves from the Li$_x$Mo$_6$Se$_z$S$_{8-z}$ cells shown in Fig. 3(b). Figure 3(a) contains results from our previous study[6] of Mo$_6$Se$_z$S$_{8-z}$ where we made the hosts by chemically removing Cu from Cu$_{2.5}$Mo$_6$Se$_z$S$_{8-z}$. We plot $-(\partial x/\partial V)_T$ versus V rather than V versus x to show more detail in the voltage behavior.[16] The data here have been normalized (to correct for particles that are electrically discon-
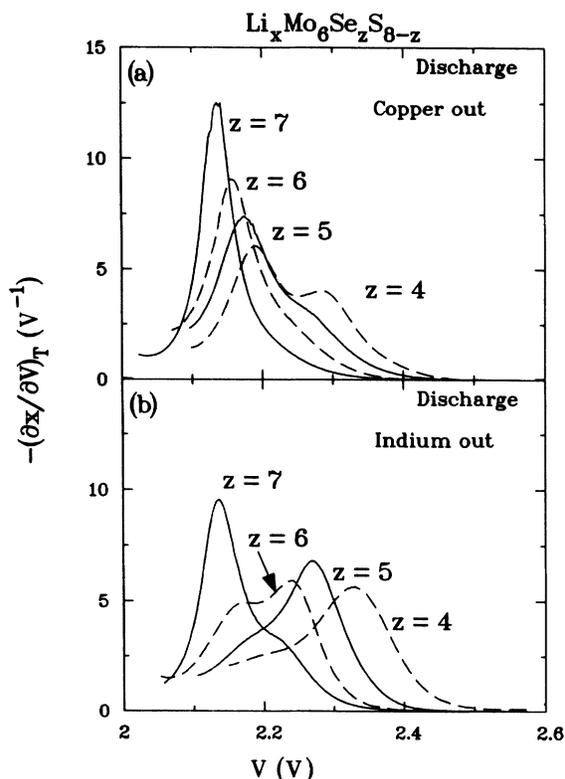
Mo.[14] The x values in this figure are calculated directly from the current passed through the cell and have not been normalized in any way.

During the first discharge of the cell, less than $x=0.01$ lithium can be added to the host before a voltage plateau at 1.8 V is reached and lithium starts to force indium out of the host. This indium displacement is similar to the displacement of copper by lithium in Li$_x$Cu$_y$Mo$_6$S$_8$ cells.[15] The plateau in voltage accompanying this displacement, at 1.8 V in Fig. 2, extends to about $x=3.5$, indicating that the indium displacement is a first-order transition, during which InMo$_6$Se$_7$S coexists with Li$_{3.5}$Mo$_6$Se$_7$S. This Li content is similar to the composition $x=4$ found in Li$_x$Mo$_6$S$_8$ (Ref. 1) and Li$_x$Mo$_6$Se$_8$ (Refs. 2 and 3) at this voltage, and in fact may well be $x=4$, because some of the compound in the cell is probably disconnected from the electrode and not intercalating Li.

If the Li$_x$InMo$_6$Se$_7$S cell is only discharged through the first plateau and then charged (data not shown), some of the indium atoms return to the Mo$_6$Se$_7$S host as the lithium is removed, accompanied by a plateau at 1.8 V. In addition, there are new voltage plateaus at higher voltages where lithium is removed from that part of the host where indium did not return. If, however, the Li$_x$InMo$_6$Se$_7$S cell is discharged below the plateau at 1.8 V, a second plateau is reached at 1.5 V as shown in Fig. 2 (labeled "first discharge"). On subsequent cycles between 2.6 and 1.2 V (labeled "first charge" and "next discharge" in Fig. 2), the plateau at 1.8 V is missing, indicating that the indium remains outside the host and does not reintercalate. Now the voltage behavior is more typical of lithium intercalating into Li$_x$Mo$_6$Se$_z$S$_{8-z}$. We have labeled the voltage plateau at 1.5 V as "indium passivation," since this plateau is associated with some reaction, with

FIG. 3. Plots of $-(\partial x/\partial V)_T$ vs voltage (V) for Li/Li$_x$Mo$_6$Se$_z$S$_{8-z}$ cells at 28 °C. These results were collected under constant current discharge between 2.6 and 2.0 V. (a) Cathode contains Mo$_6$Se$_z$S$_{8-z}$ prepared by chemical removal of copper; (b) cathode prepared with InMo$_6$Se$_z$S$_{8-z}$ and discharged below 1.2 V to remove indium before cycling in this voltage region. All the materials used in (b) were annealed 1 week at 500 °C.

nected and for side reactions of lithium with the electrolyte) to $x=1$ at the minimum in $-(\partial x/\partial V)_T$ before the long voltage plateau at roughly 1.9 V.

The curves in Fig. 3 show two peaks, one that shrinks and the other that grows as z decreases. The presence of these two peaks suggests that there are two different types of sites for the lithium in these four host materials. Following Ref. 6, we identify these sites as having seleniums on both the nearest chalcogen positions (the peak at lower voltage) or having a sulfur on one position and a selenium on the other (the peak at upper voltage). Because there is no peak near 2.45 V, there must be a negligible number of sites with sulfur atoms on both chalcogen positions. The area under each peak is proportional to the number of each kind of site. For a given z, the peak at higher voltage is larger after the indium treatment than before, suggesting that S has replaced Se in the 2c positions.

This replacement, however, proceeds slowly and is probably still continuing at 500 °C even after a week. Figure 4 shows that the Se-S peak continues to increase with further annealing. The figure shows $\partial x/\partial V$ for three samples of Mo_6Se_7S all prepared from $Cu_{2.5}Mo_6Se_7S$ in which the Cu had been removed chemically. One sample was not exposed to indium, one was annealed with indium at 500 °C for 1 week, and the third was annealed with the second and then annealed for 2 more weeks at 520 °C. (The indium was removed electrochemically from these last two samples, as in Fig. 2). The peak at 2.25 V, corresponding to sites with one Se and one S, has increased significantly after the second annealing, accounting for more than half the area under the curve. This evolution in the curves in $\partial x/\partial V$ implies that the redistribution of S and Se occurs on the time scale of weeks at 500 °C, and the final equilibrium distribution may well not have been reached even after 3 weeks.
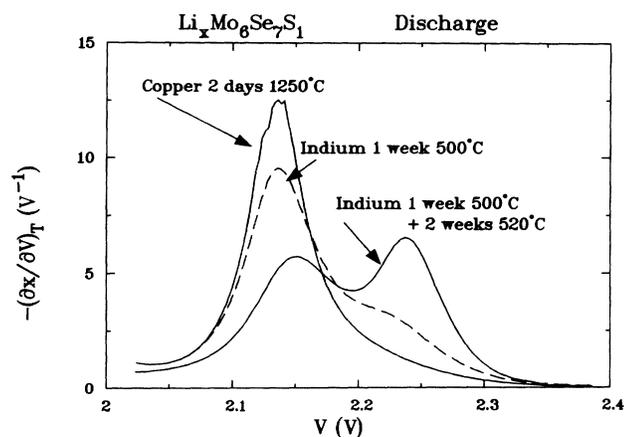

FIG. 4. $-(\partial x/\partial V)_T$ vs V from three different samples of $Li_x Mo_6Se_7S$ obtained at 28 °C on discharge. One sample was prepared with copper at 1250 °C for 2 days. Two samples were prepared with indium; both were annealed with indium at 500 °C for 1 week, and one was annealed for 2 more weeks at 520 °C.

IV. DISCUSSION

In Ref. 6 we showed that the results in Fig. 3(a) imply that there are more selenium atoms in the special 2c chalcogen positions than expected from a random distribution of sulfur and selenium. We were able to explain the relative sizes of the peaks in $\partial x/\partial V$ by assuming that the Se and S atoms are distributed over the available positions according to a lattice-gas model in which Se prefers the 2c positions. The model describes the distribution of chalcogen atoms with two parameters: z, the fraction of all chalcogen positions occupied by Se, and p, the fraction of 2c positions occupied by Se. The relationship between p and z is determined by an energy ε required to interchange a Se on a 2c position with a S on the 6f position at the temperature at which the compound is prepared.

In such a model, a chalcogen atom on one 2c position does not influence the occupation of other 2c positions, except through the constraint that a fraction z of all the chalcogen positions are occupied by Se. This assumption imposes relationships on the relative sizes of the different peaks in Fig. 3, relationships which are satisfied by the results of Fig. 3(a) and the other results from Ref. 6. Let the fraction of Li sites with 0, 1, or 2 Se atoms on 2c positions be denoted by f_0, f_1, and f_2, respectively. These fractions are related to p by

$$f_0 = (1-p)^2 \ ,$$
$$f_1 = 2p(1-p) \ , \tag{1}$$
$$f_2 = p^2 \ .$$

In Fig. 3(a), p is large for all the values of z shown, and so f_0 is too small for the third peak to be observed. But in Fig. 3(b) the f_1 peak is larger, and it is impossible to satisfy Eq. (1) with any value of the p that simultaneously allows f_1 to be so much bigger than f_2 and yet f_0 to be unobservable. Consider the worst case, the curve for $z=4$ in Fig. 3(b), for which the peak at 2.3 V (corresponding to f_1) is roughly 3 times larger than the peak at lower voltage (f_2), and so $f_2/f_1 \approx 3$. If Eq. (1) held, the second and third relations in Eq. (1) would imply $p \approx \frac{2}{5}$, which in turn would imply that the unobserved peak (f_0) should account for $(\frac{3}{5})^2 = 0.36$ of the total area, and should therefore be over twice as large as the f_2 peak.

The failure of Eq. (1) in Fig. 3(b) suggests that the rearrangement of Se and S in the presence of indium at 500 °C does not proceed according to a lattice-gas model in which the chalcogens do not interact. Some mechanism apparently inhibits two sulfur atoms from simultaneously occupying the two chalcogen positions around a given indium atom. In a lattice-gas model, such a constraint could be modeled by an interaction between the chalcogens on these two positions.

We have not pursued this model for two reasons. First, all we can conclude from Fig. 3(b) is that this interaction would have to be so large that two S atoms do not simultaneously occupy these two positions. Second, and more important, the samples in Fig. 3(b) have not reached equilibrium in a week at 500 °C, as shown in Fig. 4.

This incomplete annealing also may be behind a discrepancy between the electrochemical results of Fig. 3(b) and the structure results of Table II for $z=4$. As we discussed above, Fig. 3(b) suggests that the only types of Li sites in compounds from which indium has been removed either have two Se on the nearest $2c$ positions or have one Se and one S. If so, there should be more Se than S in the $2c$ positions. Yet the single crystal analyzed in Table II had more S than Se in these positions. Given that the powder had not fully equilibrated, perhaps the single crystal was not representative of the bulk powder.

Another possibility for this discrepancy is that the electrochemical treatment in Fig. 2 does not remove the indium from sites with sulfur in both adjacent $2c$ positions. If the S-S sites still contained indium, they would not be available to lithium and so would not be observed in the electrochemical results of Fig. 3(b). We believe this is unlikely. The voltage of the electrode in a lithium cell changes by more than 1 V, representing a strong chemical force for removing indium, and it is unlikely that indium adjacent to two sulfurs in $2c$ positions would resist this force while indium adjacent to one sulfur and one selenium does not. Moreover, we have removed indium electrochemically from $InMo_6S_8$ and $InMo_6Se_{0.8}S_{7.2}$ (using material prepared by Tarascon et al. for Ref. 10), and these higher concentrations of S do show a peak in $\partial x/\partial V$ at 2.45 V, indicating that Li is being inserted in

S-S sites. But even if indium were still present in some of the S-S sites, that would not change our main conclusion, that indium has caused the chalcogen atoms to rearrange; Fig. 3 clearly shows that there are more sites with one sulfur on the $2c$ positions after indium has been added than before.

To summarize, using results from single-crystal x-ray diffraction and electrochemical insertion of lithium in $Li_xMo_6Se_zS_{8-z}$ cells, we have confirmed that chalcogen atoms rearrange in the host at 500 °C. When the host compound is prepared as $Cu_{2.5}Mo_6Se_zS_{8-z}$ at 1250 °C and the Cu is removed chemically, there is an enrichment of selenium in the special $2c$ chalcogen position. If indium is added to $Mo_6Se_zS_{8-z}$ and annealed at 500 °C, more sulfur is found in the $2c$ positions. In addition to this rearrangement, there appears to be an interaction between the chalcogen atoms in the presence of indium; this interaction tends to prevent sulfur from occupying one $2c$ position if there is already a sulfur on the adjacent one.

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