

Entropy of the intercalation compound $\text{Li}_x\text{Mo}_6\text{Se}_8$ from calorimetry of electrochemical cells

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We describe the first measurements of changes in the entropy s of intercalation compounds from calorimetry of electrochemical cells. A lattice-gas model of intercalation accurately describes the variation of $(\partial s/\partial x)_T$ with x in $\text{Li}_x\text{Mo}_6\text{Se}_8$ at fixed temperature T with no adjustable parameters. This agreement implies that the Li atoms in $\text{Li}_x\text{Mo}_6\text{Se}_8$ for $x < 1$ are randomly distributed over a single type of site.

The entropy of most solids at room temperature arises from vibrations of the atoms about their equilibrium positions. In intercalation compounds there is also a contribution from the arrangement of the intercalated atoms over the available sites in the host. Thus, the variation of the entropy with intercalant concentration at a fixed temperature can probe the distribution of intercalated atoms.

Theoretical studies of intercalation compounds are usually based on lattice-gas models,^{1,2} where the host gives a framework of interstitial sites for intercalated atoms and mediates interactions between them. These models only consider changes in the arrangement of the intercalated atoms and not in the entropy of the host. Measurements of the entropy can be used to check the validity of such models.

Here, we report calorimetric studies of the intercalation compound $\text{Li}_x\text{Mo}_6\text{Se}_8$, studies that measure directly the entropy changes versus x at a fixed temperature T . We charge and discharge a $\text{Li}/\text{Li}_x\text{Mo}_6\text{Se}_8$ electrochemical cell in an isothermal heat-flow calorimeter and measure \dot{Q} , the heat that flows into the cell to keep the cell's temperature constant. As discussed below, \dot{Q} varies linearly with $(\partial s/\partial x)_T$, where $s(x, T)$ is the entropy per formula unit of $\text{Li}_x\text{Mo}_6\text{Se}_8$. Our results agree with the predictions of a lattice-gas model of $\text{Li}_x\text{Mo}_6\text{Se}_8$.³ In earlier work,⁴ the entropy of intercalation compounds was calculated from measurements of the voltage V of electrochemical cells from the Maxwell relation

$$(\partial s/\partial x)_T = e(\partial V/\partial T)_x + \text{const}, \quad (1)$$

where e is the magnitude of the electronic charge. Calorimetry is faster and more precise than this earlier method and allows detailed comparison of experiment and theory.

The variation of V with x and T in $\text{Li}/\text{Li}_x\text{Mo}_6\text{Se}_8$ cells for $0 \leq x \leq 1$ can be described to within the precision of experiment by a mean-field lattice-gas model.^{3,5} The success of mean-field theory implies that the interaction between Li atoms is long-ranged and that the Li atoms are randomly distributed over identical sites. For such a random distribution,

$$(\partial s/\partial x)_T = -k_B \ln[x/(1-x)] + \tilde{s}_1, \quad (2)$$

where \tilde{s}_1 is the change in s when a Li atom is added to a specified lattice site (that is, when the configurational entropy is ignored), and k_B is Boltzmann's constant. If \tilde{s}_1 is in-

dependent of x , then the dependence of $(\partial s/\partial x)_T$ on x , given by the first term in Eq. (2), has no adjustable parameters and so can easily be tested with calorimetric studies of $\text{Li}/\text{Li}_x\text{Mo}_6\text{Se}_8$ cells.

Figure 1 shows a schematic diagram of the experiment. The cell contained 5.50 g of Mo_6Se_8 powder, grown as described in Ref. 3, and was made using the "jelly-roll" construction⁶ shown in Fig. 1(a). The cell was placed in one chamber of the calorimeter and an aluminum dummy with

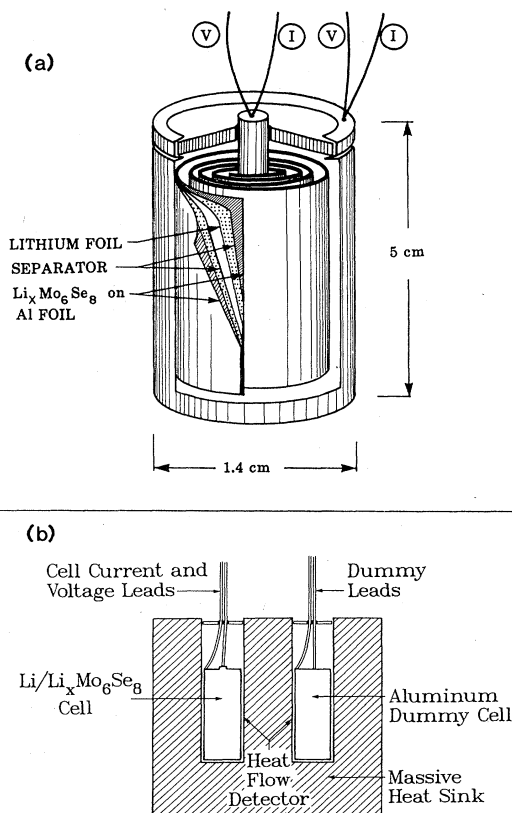


FIG. 1. Schematic diagram of the experiment: (a) the $\text{Li}/\text{Li}_x\text{Mo}_6\text{Se}_8$ cell; (b) the cell and the dummy in the calorimeter.

the same mass, size, and shape as the cell was placed in the reference chamber [Fig. 1(b)]; both cell and dummy were electrically isolated from the heat-flow detectors. We used a four-wire technique to measure the cell voltage. The calorimeter, described elsewhere,⁷ has a time constant of 200 s and a temperature stability of ± 0.002 K. The heat flow between the cell and the dummy is the measured \dot{Q} ; this differential technique minimizes extraneous heat effects.⁷

When the cell is discharged with a constant current I (intercalating Li into $\text{Li}_x\text{Mo}_6\text{Se}_8$ at a fixed rate) \dot{Q} is given by⁸

$$\dot{Q} = T[(\partial s/\partial x)_T - \bar{s}_0]N\dot{x} + \dot{Q}_0 + \dot{Q}_1 - I\eta, \quad (3)$$

where \bar{s}_0 is the entropy per Li atom in Li metal, N the number of formula units of $\text{Li}_x\text{Mo}_6\text{Se}_8$ in the cell, and \dot{x} the rate of change of x . We have added to the equation from Ref. 8 the power \dot{Q}_0 absorbed after the cell had equilibrated at zero current, the power \dot{Q}_1 absorbed by reactions other than intercalation when current flows, and the power $I\eta$ dissipated in the internal impedances of the cell, where $-\eta$ is the deviation of the cell voltage from its open-circuit value. Since $\dot{x} = I/(Ne)$, where I is positive for discharge and negative for charge,

$$e\dot{Q}/I = T(\partial s/\partial x)_T - T\bar{s}_0 + e\dot{Q}_0/I + e\dot{Q}_1/I - e\eta. \quad (4)$$

Since \bar{s}_0 is constant at fixed T , variations in $e\dot{Q}/I$ correspond to variations in $(\partial s/\partial x)_T$ if η and \dot{Q}_1 remain constant. Because N does not appear in Eq. (4), we need not know the amount of intercalation compound in the cell to obtain $(\partial s/\partial x)_T$, although we do need it to obtain x .

Figure 2 shows the voltage of the $\text{Li}/\text{Li}_x\text{Mo}_6\text{Se}_8$ cell and $e\dot{Q}/I$ vs x . These data were measured at 28.060°C while the cell was charged or discharged with a constant current at a 70-h rate. (A "70-h rate" means that it took 70 h to change x by $\Delta x = 1$ at the current used, 1.690 mA. At this rate the time constant of the calorimeter, 200 s, is negligible.) The values of $\Delta x = 0.810$ and 0.904 for the discharge and charge, respectively, were normalized to $\Delta x = 1$ to agree with previous work.^{3,5} We do not know why x was so small for the discharge, but the agreement between the measured $e\dot{Q}/I$ [Figs. 2(b) and 2(c)] for the charge and discharge implies that whatever caused this anomaly did not affect the heat flow. The results in Fig. 2 were measured after the cell was cycled to 1.6 V ($x = 4$); perhaps that affected the following discharge. Before that deep discharge, the cell had been cycled between 2.3 and 1.95 V, giving $x = 0.966$, 0.943, 0.942, and 0.960 for the first discharge, first charge, second discharge, etc., with the first two cycles measured at a 20-h rate and the last discharge at a 70-h rate.

The open circles in Figs. 2(b) and 2(c) were calculated from Eq. (2): to align theory and experiment, we shifted the calculations by -3.1 and $+24.1$ meV for discharge and charge, respectively. The agreement between theory and experiment in Fig. 2 implies that the Li randomly occupies a single type of lattice site; we discuss the differences near $x = 0$ and $x = 1$ below. The offsets needed to align theory and experiment are related to \bar{s}_1 and the last four terms in Eq. (4): if \dot{Q} is the same on charge and discharge, the difference in the offsets, -27.2 meV, is $(2e\dot{Q}_1/I) + (2e\dot{Q}_0/I) - 2\eta$, and the average of the offsets, 10.5 meV, is $T\bar{s}_1 - T\bar{s}_0$. We measured $\dot{Q}_0 = -11 \pm 5 \mu\text{W}$, which for this cell was equal to the zero offset of the calorimeter. The value of η can be estimated from the shift between $V(x)$

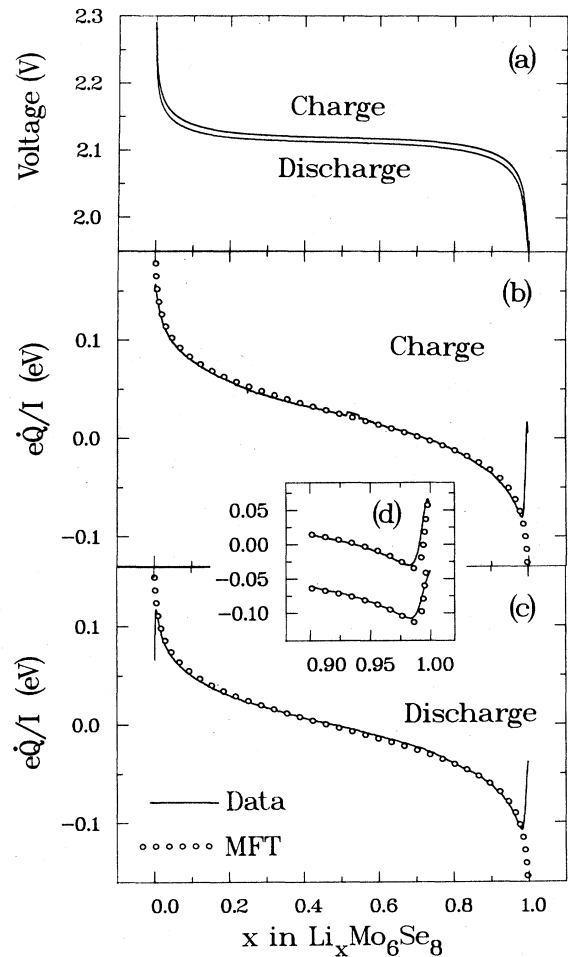


FIG. 2. Results of the calorimeter experiment on an $\text{Li}/\text{Li}_x\text{Mo}_6\text{Se}_8$ cell at 28.060°C . (a) Voltage vs x during charge and discharge at a 70-h rate. (b) $e\dot{Q}/I$ measured during charge (—, experiment; O, theory), (c) As in (b) except for discharge. We believe the small step near $x = 1$ in (b) was produced by a dendrite of Li that grew through the separator in the cell; power dissipated by current flowing through the dendrite increased the heat flow from the cell until the dendrite disappeared. (d) An enlargement of the data near $x = 1$ compared with the predictions of the theory with the parallel capacitance (see text). The upper curve is for charging and has been offset by 50 meV for clarity. Each of the data sets above has over 2000 data points. Although the theoretical expressions are analytic, for clarity we have plotted points.

for the charge and discharge in Fig. 2(a); this gives $2\eta = 6.89$ mV, which corresponds to an impedance of $\eta/I = 2.04 \Omega$ and to a power $I\eta = 5.8 \mu\text{W}$. From η and \dot{Q}_0 , we find the value of \dot{Q}_1 averaged between charge and discharge is $\dot{Q}_1 = 6 \mu\text{W}$. These values are small compared with powers as high as $150 \mu\text{W}$ generated and absorbed during intercalation. It is thus reasonable to neglect differences in \dot{Q}_1 between charge and discharge. Using $\bar{s}_0 = 0.290$ meV/K,⁹ we find $\bar{s}_1 = 0.33 \pm 0.01$ meV/K. \bar{s}_1 arises from vibrations of the Li atom in its site as well as changes in the entropy of the host. Because the term from the configurational entropy in Eq. (2) describes the variation with x of Figs. 2(b) and 2(c), any changes in the entropy of the host must be linear in x .

The behavior in Figs. 2(b) and 2(c) near $x=0$ and $x=1$ can be modeled by a small capacitance charging in parallel with intercalation. The effective capacitance of intercalation, $-(\partial x/\partial V)_T$, becomes small near $x=0$ and $x=1$. Here, most of the current is charging the parallel capacitance, not intercalating $\text{Li}_x\text{Mo}_6\text{Se}_8$, so the heat output falls. Figure 2(d) shows how including a capacitance of 0.05 V^{-1} in the theory gives good agreement with the data near $x=1$. (The $x=0$ case is similar, although the parallel capacitance is only about half as large as near $x=1$.) A capacitance of 0.05 V^{-1} , although much smaller than $-(\partial x/\partial V)_T$ except near $x=0$ or $x=1$, is too large to be explained by the capacitance of the electrical double layers at the electrolyte-electrode interfaces.¹⁰ Li fills other sites in the host for $x > 1$, and some of these sites will be occupied for $x < 1$. We have included this second site in lattice-gas models and find that it contributes to the rounding of the data near $x=1$ but not near $x=0$. We do not know the origin of this extra capacitance.

Figure 3 shows $-(\partial x/\partial V)_T$ vs x from Fig. 2(a). The similarity of the charge and discharge shows that at 70-h rates the potential η is almost constant. Also shown is the prediction of mean-field theory³

$$-(\partial x/\partial V)_T = 1/\{U + kT/[x(1-x)]\}, \quad (5)$$

with $U = -0.0914 \text{ eV}$. Here, U/N is the energy of interaction between any two intercalated Li atoms in the host. This value of U , which gives the best fit to the data in Fig. 3, is 1% larger in magnitude than the value reported in Ref. 3, -0.0904 eV . This small difference might be due to differences in the host compound; the material in these experiments was grown in a different batch from that used in Ref. 3.

The agreement in Figs. 2(b) and 2(c) shows that the variation of the entropy of $\text{Li}_x\text{Mo}_6\text{Se}_8$ can be described by a lattice-gas model. The only changes in the entropy of the Mo_6Se_8 host are linear in x . The host can thus be considered a passive framework, which mediates interactions between intercalant on different sites, and into which intercalant can be inserted.

In the rigid-band picture of intercalation,² an intercalated Li atom donates its $2s$ electron to the host. Several authors¹¹ have considered the electron and the ion to be in-

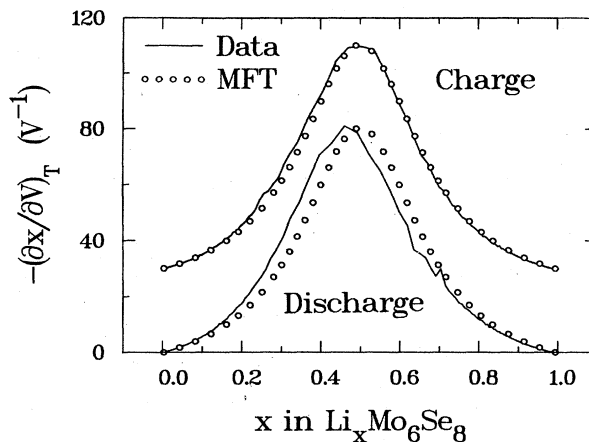


FIG. 3. $-(\partial x/\partial V)_T$ vs x for the cycle shown in Fig. 2(a) (—), and the predictions of mean-field theory for $U = -0.0914 \text{ eV}$ (○). The charge has been offset by 30 V^{-1} for clarity.

dependent and find $(\partial s/\partial x)_T$ to be twice that given by Eq. (2). Since Eq. (2) describes $\text{Li}_x\text{Mo}_6\text{Se}_8$, the Li must be regarded as a neutral atom, at least in calculations of the entropy. Perhaps Li donates its $2s$ electron to the host bands, but the Li ions polarize the host electrons so that the ion plus its polarization cloud is neutral. Such a polarization is found in calculations of the electronic structure of Li_xC (Ref. 12) and Li_xTiS_2 .¹³

The voltage of an intercalation cell measures the chemical potential μ of the intercalated species in the host,² and the rate of heat flow in a calorimeter experiment measures $T(\partial s/\partial x)_T$. If both μ and $T(\partial s/\partial x)_T$ are known with high precision, then $(\partial h/\partial x)_T$, where h is the enthalpy of the intercalation compound, can be calculated from their difference. [$(\partial h/\partial x)_T$ calculated in this way for $\text{Li}_x\text{Mo}_6\text{Se}_8$ for $x < 1$ is just $-Ux$.] Separating the enthalpy and the entropy from μ has allowed us to understand the structural transition in $\text{Li}_x\text{Mo}_6\text{Se}_8$ (Ref. 5) near $x=3.7$; these results will be published elsewhere. We expect that similar studies on other intercalation compounds will assist in understanding their behavior.

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