

UNDERSTANDING THE BEHAVIOUR OF RECHARGEABLE LITHIUM BATTERIES (EXTENDED ABSTRACT)

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Unlike common nickel-cadmium or lead-acid batteries, the voltage of most lithium cells with insertion electrodes usually varies significantly with the cell's state of charge [1]. Many researchers have measured these variations and have used various phenomenological models to try to understand them. Here, we review several examples of our work where high quality electrochemical and structural data have been explained with reasonable models. The models also allow predictions of the phase diagrams of intercalation compounds to be made.

The lattice-gas model is that most commonly used to describe intercalation compounds [2 - 4]. In this picture, the host has two roles: it provides a lattice of sites where guest atoms reside and it determines the interactions between the guest atoms. These interactions are complicated: they consist of coulomb interactions screened by the host and elastic interactions caused by the distortion of sites by the guest. Because it is hard to calculate such interactions from first principles, they are usually taken as model parameters. We shall discuss several systems where lattice-gas models have been especially successful.

The voltage curve, $V(x)$, of $\text{Li}/\text{Li}_x\text{Mo}_6\text{Se}_8$ cells is well fitted by a simple cubic lattice-gas model solved using mean field theory [5]. In this approximation, the chemical potential, μ , and the voltage, V , are:

$$\mu = -eV = E_0 + \gamma Ux + kT \ln(x/(1-x)) \quad (1)$$

Here E_0 is the energy associated with the filling of an isolated lattice site, γ is the number of sites coupled to a given site by the interaction U , k is Boltzmann's constant and T is the Kelvin temperature. Figure 1(a) shows the data measured at 38 °C, and the theoretical prediction with $E_0 = -2.35$ eV, and $\gamma U = -0.0904$ eV (from ref. 5). The differential capacity, $-dx/dV$ is easily calculated by differentiating eqn. (1).

Figure 1(b) shows the agreement between the data and the theory.

The agreement of the mean field expressions imply that $\text{Li}_x\text{Mo}_6\text{Se}_8$ is a single phase at room temperature. Figure 2 shows portions of X-ray diffrac-

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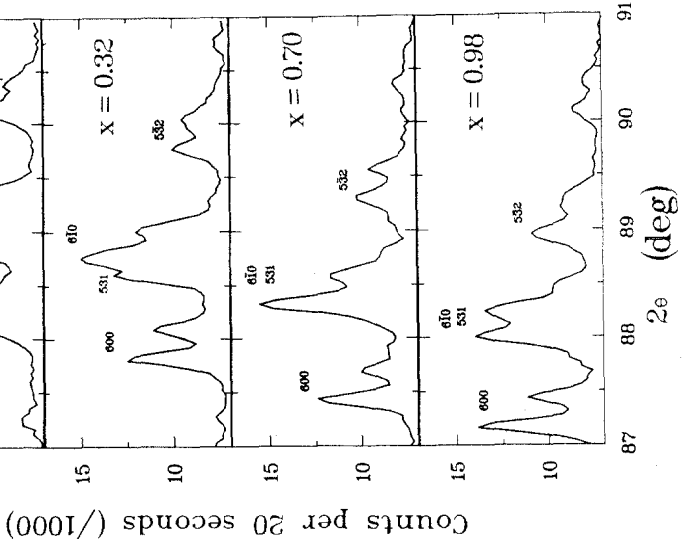


Fig. 2. X-ray diffraction profiles of $\text{Li}_x\text{Mo}_6\text{Se}_8$ taken at $x = 0, 0.32, 0.70$ and 0.98 . The peaks are labeled by their rhombohedral Miller indices.

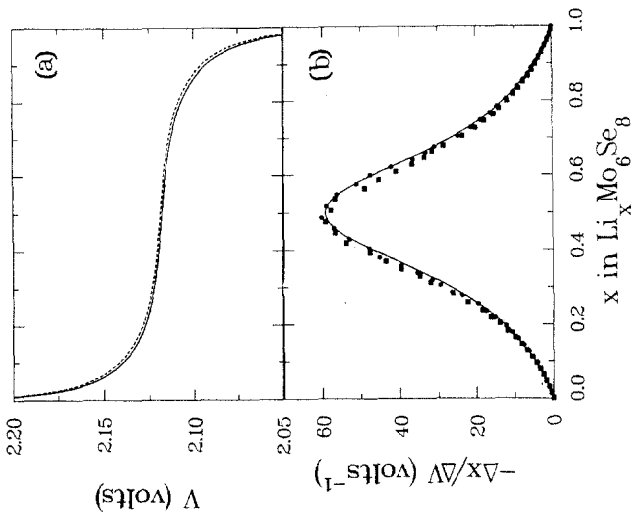


Fig. 1. (a) $V(x)$ for an $\text{Li}/\text{Li}_x\text{Mo}_6\text{Se}_8$ cell at 38°C ; the solid line denotes discharge, and the dashed line denotes charge. (b) $-\Delta x/\Delta V$ vs. x from (a). The solid curves are the theoretical predictions.

tion profiles taken at $x = 0, 0.32, 0.70$ and 0.98 using an *in situ* X-ray diffraction method [6, 7]. The Bragg peaks simply shift as Li is added; at all compositions the X-ray diffraction profiles can be explained by the presence of a single phase. Figure 3 shows the lattice constants measured using *in situ* X-ray diffraction.

The theoretical expressions predict that dx/dV is temperature dependent. Figure 4 shows the data collected at 38, 28 and 15 °C and the prediction of the theory using $\gamma Y = -0.0904$ eV [5].

The theory predicts that phase separation should occur when $-dx/dV$ diverges for $T < T_c \equiv |\gamma U|/4k = 267$ K. Using an *in situ* X-ray cell mounted on a thermostat, we have confirmed this phase separation [8]. Figure 5(a) shows the 411 Bragg peak of $\text{Li}_{0.48}\text{Mo}_6\text{Se}_8$ measured at several temperatures. Figure 5(b) shows the same data with the $K\alpha_2$ peaks deconvoluted. It is clear that for $T < 260$ K, phase separation has occurred.

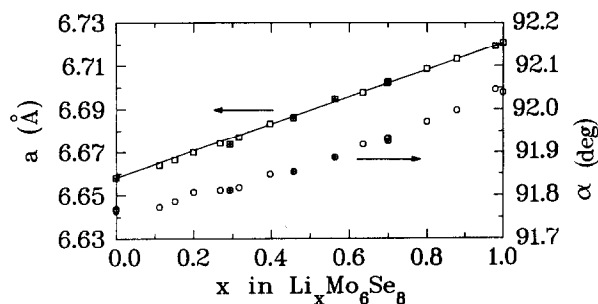


Fig. 3. Variation of the lattice parameters a (squares) and α (circles) of $\text{Li}_x\text{Mo}_6\text{Se}_8$ as determined by *in situ* X-ray diffraction.

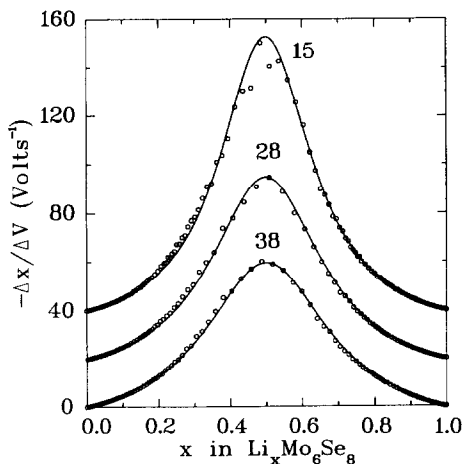


Fig. 4. $-dx/dV$ vs. x for $\text{Li}/\text{Li}_x\text{Mo}_6\text{Se}_8$ cells at 15 °C, 28 °C and 38 °C. The solid lines are the predictions of the theory. The data and calculations for 28 °C and 15 °C have been offset by 20 and 40 V^{-1} , respectively, for clarity.

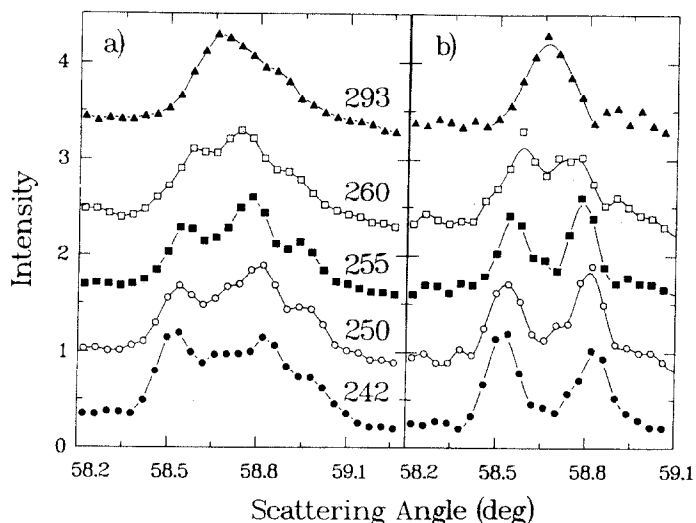


Fig. 5. (a) The $(41\bar{1})$ Bragg peak of $\text{Li}_{0.48}\text{Mo}_6\text{Se}_8$ at 242, 250, 255, 260, and 293 K. (b) Same as in (a) except that the $K\alpha_2$ peaks have been removed.

These results prove conclusively that $\text{Li}_x\text{Mo}_6\text{Se}_8$ is a model — mean field lattice gas for $0 \leq x \leq 1$. The success of mean field theory in describing $\text{Li}_x\text{Mo}_6\text{Se}_8$ implies that the attractive Li–Li interaction is of long range and is probably caused by the strain fields set up by intercalated Li atoms.

Although most other intercalation components are more complex than $\text{Li}_x\text{Mo}_6\text{Se}_8$, we will also discuss two other cases, Li_xTiS_2 and $2\text{H-Li}_x\text{TaS}_2$, where lattice gas models have been successfully applied to explain the physics and chemistry of intercalation.

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