

The entropy and enthalpy of lithium intercalation into graphite

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Abstract

Measurements of open-circuit voltages (OCV) in half-cells with graphite electrodes were used to obtain the entropy and enthalpy of lithium intercalation into graphite. At low lithium concentrations, the entropy included a component identified as an entropy of mixing. The entropy of intercalation changed sign at higher lithium concentrations, suggesting a second component. Raman spectroscopy and prior work on inelastic neutron scattering indicate that this additional entropy is vibrational in origin. The enthalpy of intercalation into graphite is consistently negative, but becomes less so with higher lithium concentrations.

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1. Introduction

Thermodynamic data are straightforward to acquire from equilibrated electrochemical cells. In particular, the open-circuit voltage (OCV) of a half-cell of graphitic Li_xC_6 against Li metal is a direct measure of the difference of chemical potential for a lithium atom in the Li metal and in the graphite [1]. The temperature-dependence of this OCV, E_0 , provides the entropy of intercalating additional Li into the Li_xC_6 as

$$\Delta S(x) = F \left. \frac{\partial E_0}{\partial T} \right|_x, \quad (1)$$

where F is the Faraday constant and T is the temperature. The term $-T \Delta S$ can be subtracted from the OCV to obtain the enthalpy of intercalation (at the Li concentration, x), $\Delta H(x)$:

$$\Delta H(x) = -FE_0(x, T) + T\Delta S(x). \quad (2)$$

In this paper, by $\Delta S(x)$ and $\Delta H(x)$ we mean the change in entropy and enthalpy that occur as an amount of lithium, Δx , is intercalated into the graphite. The reference for $\Delta S(x)$ and $\Delta H(x)$ is the bcc lithium metal plus the partially-intercalated graphite of composition $x - \Delta x$.

We report that the entropy of intercalation of lithium into Li_xC_6 is large and positive at low lithium concentrations, $x < 0.2$. This is explained as originating with a change in configurational entropy. The entropy of intercalation becomes

negative at higher lithium concentrations of $x > 0.2$. This requires a second contribution, which we argue is vibrational in origin. The enthalpy of intercalation, $\Delta H(x)$, is negative for all x . The $\Delta H(x)$ is less negative when forming the stage-1 compound LiC_6 from the stage-2 compound LiC_{12} , indicative of a repulsive lithium–lithium interaction at high lithium concentrations.

2. Experimental

Coin cells of 20 mm diameter and 1.6 mm thickness (CR 2016-type) were used as test half-cells in this study. Cells consisted of metallic lithium as counter (and reference) electrodes, a microporous polyethylene separator soaked with 1M solution of LiPF_6 in equi-volume mixture of EC and DMC, and a composite graphite electrode. The later was prepared by casting onto a PTFE substrate a suspension in acetone of 75 wt.% of graphite powder (Superior Graphite Co., USA, ref. SO-3-24-1), 15 wt.% of PVDF (AtoFina, France, ref. 2801) and 10 wt.% of acetylene black (PUK, France, Y-grade). This was followed by drying in air at ambient temperature and in vacuum at 80 °C for overnight. Electrodes of 14 mm diameter and of about 10 mg in weight were cut from the film. The graphite electrode was pressed on a stainless steel spacer before assembling the coin cell in an argon-filled dry box. The coin cells were cycled from 0.0 to 1.5 V five times at a $C/5$ rate. Cyclic voltammetry was then performed at a slow sweeping rate of $5 \mu\text{V s}^{-1}$ to identify the voltages at which equilibrium phases are formed in the graphite. For the measurements of thermodynamic properties,

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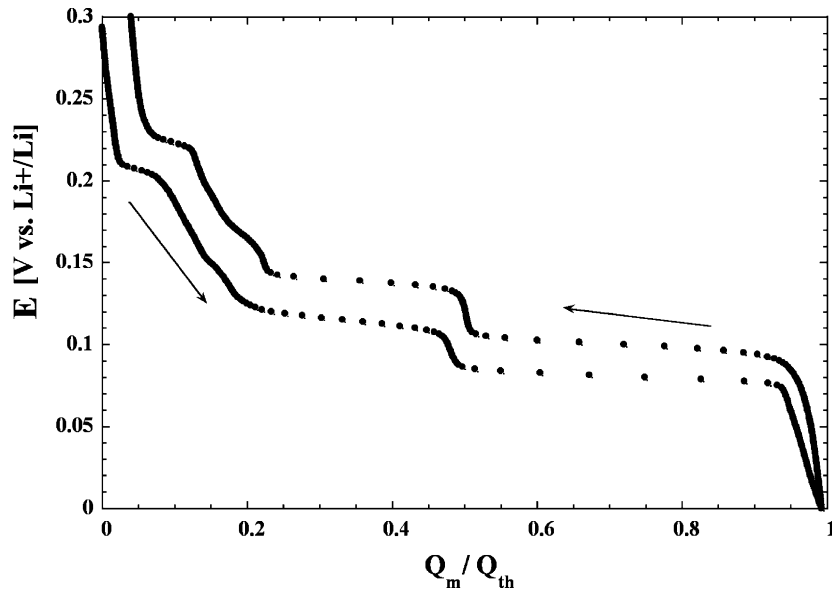


Fig. 1. Voltage vs. composition from cyclic voltammetry performed at a $C/50$ rate at $23\text{ }^{\circ}\text{C}$.

an electrically-insulated cell was placed in a thermal water bath and its open-circuit voltage was measured after thermal equilibration was achieved. The temperature was increased from near $0\text{ }^{\circ}\text{C}$ to typically $23\text{ }^{\circ}\text{C}$ in approximately $5\text{ }^{\circ}\text{C}$ intervals, and five OCV measurements were made on the cell at thermal equilibrium. The graphite was then delithiated slightly at $23\text{ }^{\circ}\text{C}$ with a $C/50$ rate, and another set of OCV versus T data was obtained. Complete sets of data were acquired for two coin cells, and the results were in good agreement.

Chemically lithiated HOPG was used for the Raman scattering measurements. The specimen was removed from

the molten lithium bath at $220\text{ }^{\circ}\text{C}$ before lithiation to LiC_6 came to completion. The sample showed areas with easily distinguishable golden (dominant), blue (small) and purple (minor) colors corresponding to stage-1, stage-2 and very likely to fractionary-stage compounds, respectively. The latter was found at boundary areas between the golden and the blue colored phases. The lithiated HOPG sample was protected from air with a thin glass slide hermetically glued to a thicker glass support with a vapor-free sealant inside a dry box filled with argon.

Raman spectra were recorded on a multichannel XY Dilor spectrometer using an argon ion laser source with a 514 nm

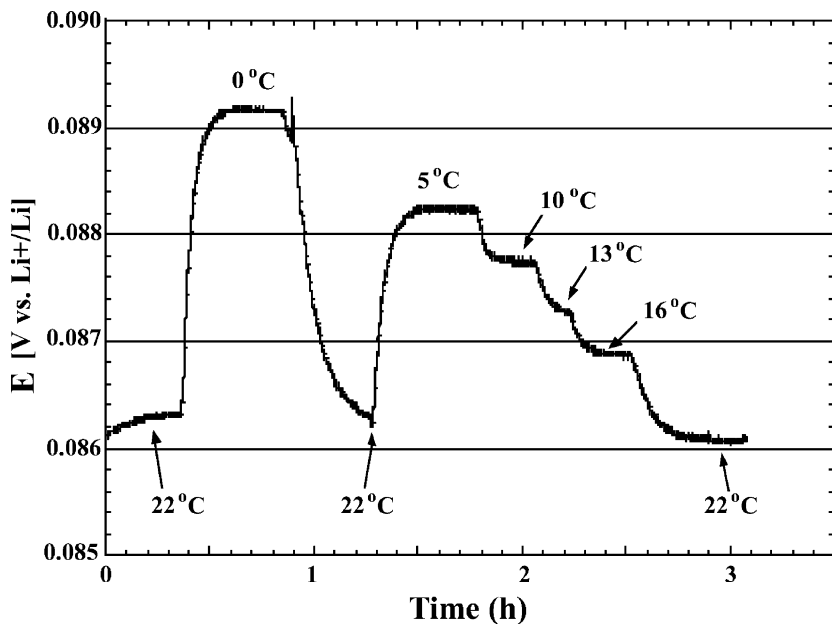


Fig. 2. Typical OCV measurements, showing voltage vs. time. At various times the temperature of the thermal bath was changed abruptly. Temperatures of equilibration are shown as labels.

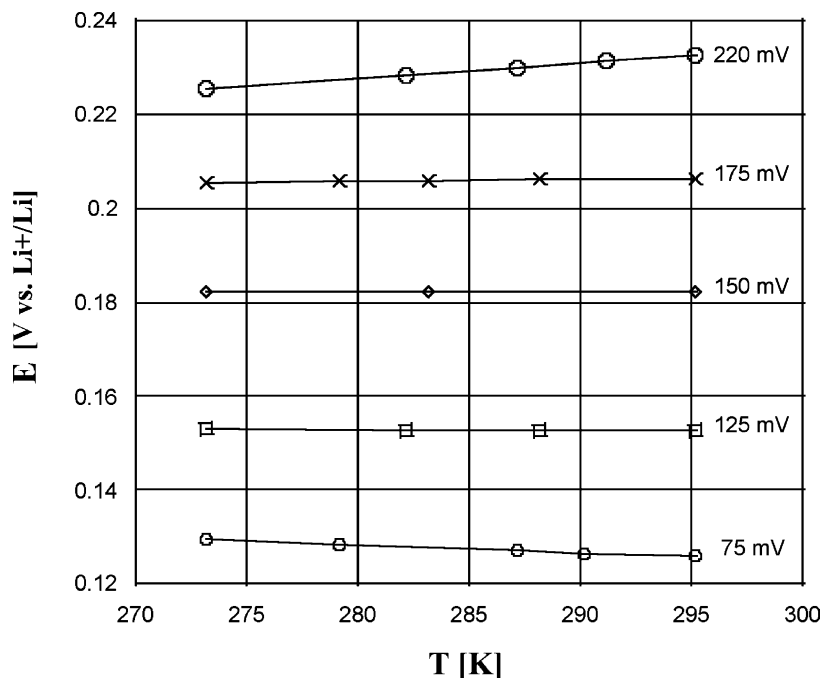


Fig. 3. Open-circuit voltage vs. temperature, measured at different states of lithiation. The curves are labeled by equilibrium voltage at 23 °C, corresponding to compositions on the X-axis of Fig. 1.

wavelength. The laser power at the sample was limited to 4 mW to avoid heating the sample. The spectrometer was coupled to an optical microscope and was used in the backscattering configuration. An 'X50' objective was used so as areas of 1.1 μm in diameter could be probed. This made it easy to select areas on the lithiated HOPG specimen with defined intercalation stages.

3. Results

A graph of the open-circuit voltage versus lithium concentration (OCV versus x), derived by integrating a cyclic voltammogram measured at a $5 \mu\text{V s}^{-1}$ sweeping rate, is presented in Fig. 1. Note the distinct plateau from $x = 0.5$ – 0.9 , corresponding to the formation of the stage-1 graphite

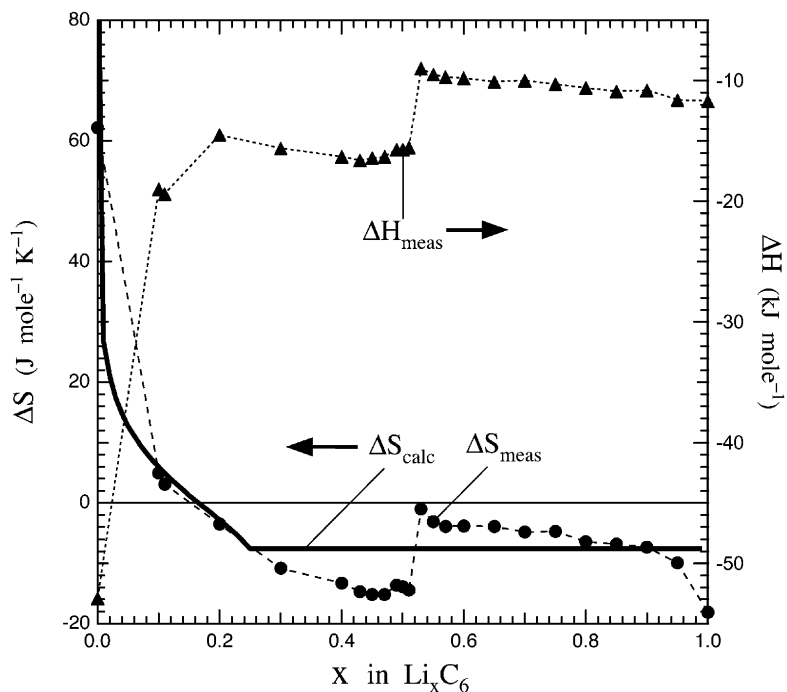


Fig. 4. Composition-dependence of the entropy and enthalpy of intercalation, $\Delta S(x)$ and $\Delta H(x)$, as defined in text. Labels ΔS_{meas} and ΔH_{meas} refer to the experimental data, the label ΔS_{calc} refers to the calculation of the entropy of intercalation (see text).

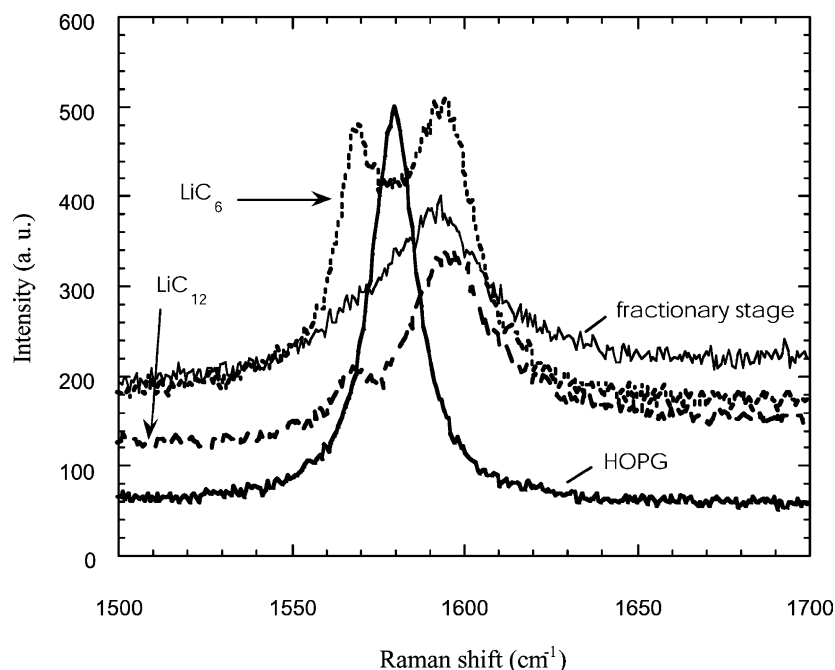


Fig. 5. Micro-Raman spectra of pristine HOPG and HOPG-based LiC_{12} , LiC_6 and fractionary-stage material.

intercalation compound (GIC) LiC_6 , and the plateau from $x \sim 0.25$ – 0.5 , corresponding to the formation of the stage-2 GIC LiC_{12} . Staging is not obvious for $x < 0.25$. Fig. 2 shows typical data from OCV measurements. After each abrupt change in the thermal bath, both the temperature of the cell and the OCV reached equilibrium values in approximately 30 min. Notice that the OCV decreases with temperature, indicating from Eq. (1) that $\Delta S < 0$. Five data sets like those of Fig. 2 were used to obtain the five curves of Fig. 3. Notice that the negative slope changes sign to positive slope at higher cell voltages, corresponding to $\Delta S > 0$ at small lithium concentrations. From the slopes and the Y -axis intercepts of the lines like those in Fig. 3, ΔS and ΔH were obtained at various x , and these results are plotted in Fig. 4. These results are in good agreement with recent results of Thomas and Newman [2].

Fig. 5 shows the Raman spectra of the pristine HOPG together with stage-1 LiC_6 , stage-2 LiC_{12} and the fractionary stage. The frequency of the in-plane Raman-active E_{2g_2} mode is a singlet at 1580 cm^{-1} for the pristine HOPG and a doublet for LiC_6 at 1569 and 1593 cm^{-1} as well as for LiC_{12} at 1569 and 1596 cm^{-1} . For the fractionary stage, a broader peak is obtained with a maximum position at 1592 cm^{-1} .

4. Discussion

4.1. Raman scattering

Raman spectrometry is an appropriate tool for local studies especially in disordered materials and/or in minor

phases. The doublet structure of the Raman spectra at frequencies close to the E_{2g_2} mode was reported and discussed in the early Raman work on donor- and acceptor-type graphite intercalation compounds [3,4]. The Raman spectrum provides evidence for the fractionary-stage, whereas this phase would be difficult to detect by X-rays diffraction (owing to very weak intensity of the $(h k 0)$ diffraction peaks in HOPG- Li_xC_6 and to the small fraction of the phase). The peak broadening of the fractional-stage is the signature of composition and/or structure disorder in the compound, which affects the entropy of the Li_xC_6 phases as will be discussed in the next Section 5.

4.2. Entropy of intercalation

The ΔS of Eq. (1) is the entropy of formation of an additional amount of intercalation compound, taking lithium from bcc metal (of constant entropy per mole of lithium), and placing it into graphite in various states of lithiation. In these non-magnetic materials, there are three possible sources for the entropy of formation, originating with three independent degrees of freedom within the materials—configurational, vibrational, and electronic.

The configurational entropy is zero for the initial materials, bcc lithium and hexagonal graphite crystals, because the orientation of one unit cell dictates the positions of all atoms in the crystals. Ordered graphite intercalation compounds (GICs) also have zero configurational entropy for the same reason. For example, in forming a well-ordered stage-1 compound LiC_6 from a well-ordered stage-2 compound LiC_{12} , two well-ordered crystals exist side by side. The entropy associated with the boundaries between them is

negligible unless the GICs are nanocrystalline. Configurational entropy should be large at small concentrations of lithium, because there are so many equivalent sites for placing lithium atoms in the disordered intercalation compounds. The composition derivative of the configurational entropy of mixing is

$$\frac{dS_{\text{config}}}{dx} = -k_B \ln \left[\frac{(x_0 - x)}{x} \right], \quad (3)$$

where the solubility limit of the disordered phase is x_0 , and Eq. (3) is valid only for $x < x_0$.

For low lithium concentrations when $x < x_0$, Eq. (3) provides a major contribution to the entropy of adding an increment of lithium, dx . It seems that approximately $x_0 = 0.25$ for our graphite. For compositions $x > x_0$, Fig. 1 shows two flat plateaus, corresponding to a constant chemical potential as LiC_{12} and LiC_6 are formed. Note in Fig. 4 that ΔS is negative for $x > 0.2$. The bcc Li has zero configurational entropy. A negative ΔS_{config} of formation could exist over a range of x , if the new phase has a smaller configurational entropy than the phase it replaces, but this argument is quantitatively unsuccessful with the data of Fig. 4. When replacing all the LiC_{12} with LiC_6 from $0.5 < x < 0.95$, the negative entropy requires that the original LiC_{12} would have a ΔS_{config} of about $0.5 k_B/\text{atom}$. This is typical of a disordered solid solution, not a well-ordered GIC. Additionally, the entropy versus composition curves of Fig. 4 and especially of [2] are flat over wide ranges of composition, a behavior that is not typical of configurational entropy.

It is now known that differences in the vibrational entropy between different solid phases are a major source of the entropy of solid–solid phase transformations [5,6]. The vibrational entropy depends on all phonon frequencies of the solid, but it is common to extract a Debye temperature from a measured phonon spectra. A Debye temperature is a convenient but approximate parameterization for the phonon energy spectrum when the spectrum itself is not available in numerical form. Typical experimental analyses of the vibrational spectra of intercalated lithium atoms provide two Debye temperatures, a $\theta_{D\perp}$ for the one dimension of lithium motions normal to the graphene planes, and a $\theta_{D\parallel}$ for the two dimensions of lithium motions along the plane of the graphene sheets. With a Debye temperature θ_{D0} for bcc Li metal, we obtain the vibrational entropy of formation:

$$\Delta S_{\text{vib}} = 1 k_B \ln \left(\frac{\theta_{D0}}{\theta_{D\perp}} \right) + 2 k_B \ln \left(\frac{\theta_{D0}}{\theta_{D\parallel}} \right). \quad (4)$$

For both LiC_{12} and LiC_6 , we use $\theta_{D\perp} = 893$ and $\theta_{D\parallel} = 392$ K from calculations in the literature [7]. The $\theta_{D\parallel}$ is consistent with measurements by Schirmer et al. [8] for the phonon partial density of states (DOS) of lithium atoms. For bcc lithium metal we use an experimental $\theta_{D0} = 380$ K [9]. We assume that the carbon phonon modes are not affected significantly by the intercalation of lithium, but this approximation is discussed further below.

By adding an additional amount of lithium, dx , to an intercalated graphite of composition x , we used the configurational entropy from Eq. (2) plus the vibrational entropy of Eq. (4) to obtain the calculated entropy presented in Fig. 4. In doing so, we used a composition range for the disordered phase of x from 0 to 0.25, and assumed that the staged compounds LiC_{12} and LiC_6 were in the composition ranges of 0.25–0.5 and 0.5–1.0, respectively. This calculation with configurational entropy plus vibrational entropy can explain the change of sign of ΔS versus x . The ΔS becomes negative for $x > 0.2$ because the vibrational frequencies of lithium atoms perpendicular to the graphene planes are quite high. Interestingly, the average vibrational frequencies parallel to the graphene planes are similar to those in lithium metal. When lithium is intercalated into graphite, the lithium atoms are restricted in their movements normal to the graphene planes, and explore a smaller range of displacements than in lithium metal. The change in vibrational entropy with intercalation is therefore negative.

The experimental data show a change in entropy at the transition between stage-1 and stage-2 compounds ($x = 0.5$), but this is not predicted by our model. We assumed the same configurational and vibrational entropy per mole of stage-1 and stage-2 compounds because we do not have enough information to reliably do otherwise, but both assumptions could be questioned. For example, there is the possibility that the stage-1 compound is not fully ordered, so a small increase in configurational entropy might be expected at $x = 0.5$. If the transition from stage-2 to stage-1 involves some fractionary stages, or involves a lower density stage-1 compound [10], some increase in configurational entropy would occur, but it seems that this is not large. The vibrational entropy may also be expected to change at $x = 0.5$ because the stacking of the graphene layers is altered. Evidence for changes in the phonon modes involving lithium atoms is incomplete. The lithium vibrations may be stiffer in the stage-1 compound than in the stage-2 [11], suggesting a change of ΔS at $x = 0.5$ of the opposite sign to the data of Fig. 4, but the phonon data sets are not quite comparable.

The phonon modes of the carbon atoms are distinctly different for the stage-1 compound, and this involves a small number of lithium atoms per carbon atom. The Raman data of Fig. 5 provide information on only one vibrational mode, and as such they cannot be used to assess the change in vibrational entropy of the stage-2 to stage-1 transition. They do, however, show that significant changes in the carbon motions do occur with lithiation. We therefore believe that a change in vibrational entropy could contribute to the change in ΔS at $x = 0.5$ that is seen in the experimental data of Fig. 4, but we do not know how to quantify it from the data available to us.

Electronic entropy is thermodynamically important in actinide elements (for the β - γ phase transition in uranium, $\Delta S_{\text{el}} = 4.5$ J/(mole K) [12]) and it makes a small contribution

to transition metals. For intercalated graphite, however, we expect this contribution to be much smaller.

4.3. Enthalpy of intercalation

The enthalpy of intercalation, ΔH , is negative, as expected from the positive voltages of Fig. 1. Approximately, the formation of LiC_{12} occurs with a ΔH of -17 kJ/mole, and LiC_6 forms with a somewhat less favorable ΔH of -11 kJ/mole. We note that these numbers are actually rather small—the enthalpy of lithium in graphite and of lithium in bcc lithium metal are similar. In earlier work, it was shown that lithium atoms are essentially neutral atoms when intercalated into graphite [13], so a typical Coulomb interaction energy of -100 kJ/mole is not expected, nor are large differences expected in the Coulomb interaction energy of LiC_{12} and LiC_6 . In LiC_6 , the stacking sequence of the graphene and the lithium layers is $A\alpha A\alpha A\alpha$. The Li–Li distance is a 372 pm along the c -axis and a 426 pm within the plan. Such data are not compatible with repulsive interactions of purely ionic nature but suggest instead a metallic character of the Li–Li bondings as stage-1 LiC_6 forms.

5. Conclusions

The enthalpy and entropy of the intercalation of lithium into graphite were obtained by measuring the temperature-dependence of the open-circuit voltages of half-cells of $\text{Li}/\text{EC}\text{-DMC} + \text{LiPF}_6/\text{graphite}$. At lithium concentrations $x < 0.25$ in Li_xC_6 , the entropy is dominated by a configurational component. The negative value of the entropy of intercalation at lithium concentrations of $x > 0.25$ in Li_xC_6 can be explained by a vibrational contribution because phonon data on lithium in graphite, taken from the literature, show that lithium atom vibrations in graphite are at higher frequencies than in lithium metal. The enthalpy of inter-

calation is negative, with ΔH of -17 kJ/mole for LiC_{12} and -11 kJ/mole for LiC_6 , indicative of a greater repulsive contribution of Li atoms in the stage-1 compound.

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