The Entropy of Intercalation of Li into Li_xCoO_2

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The entropy of lithiation of Li_xCoO_2 for $0.5 < x < 1.0$ was determined from measurements of the temperature-dependence of equilibrated voltages of electrochemical cells. Changes in the entropy of the lithiation reaction were as large as 9.0 k_B/atom, and as large as 4.2 k_B/atom within the layered hexagonal structure of Li_xCoO_2. Three contributions to the entropy of lithiation for the layered hexagonal phase were assessed by experiment and calculation.

The $LiCoO_2$ powders were prepared by Enax Inc., and foil cathodes containing 91% active material were also provided by Enax Inc. The open circuit voltages of Li/Li_xCoO_2 half cells were measured as functions of temperature at various lithium concentrations to determine the entropy of the lithiation reaction. The 2016 coin cells for electrochemical measurements used a microporous polyethylene separator, and an electrolyte of molar $LiClO_4$ in polyethylene carbonate.

The phonon entropy of lithiation was determined from measurements of inelastic neutron scattering. The samples used in the inelastic neutron scattering experiments were prepared by chemical delithiation of Li_xCoO_2 powder using an aqueous solution containing different concentrations of potassium persulfate ($K_2S_2O_8$). X-ray diffractometry was used to determine the lattice parameters and estimate the compositions of these delithiated materials. Inelastic neutron spectra were acquired with the Pharos instrument, a time-of-flight chopper spectrometer at the Los Alamos Neutron Scattering Center, LANSCE. Independent sets of data were acquired from neutron beams having incident energies of 147 meV and 243 meV at ambient pressure and room temperature. Data were corrected for incident flux, background and intensity. For each angle bank, the one-phonon double-differential cross-section was isolated using an iterative process [1]. The final result is a phonon density-of-states, with some distortion from the differences in phonon scattering efficiencies of Li, Co, and O. The data shown in figure 1 include a large peak at around 155 meV for the samples that were delithiated in an aqueous medium. This peak corresponds to OH or H_2O vibrational modes, and should be ignored. The overall changes with lithium concentration were found to be small.

The electronic structure calculations were performed with the ab-initio total energy and molecular dynamics program VASP [2]. The electronic density of states showed the Fermi level to lie at the band gap for the insulating phase of high lithiation, as expected. The electronic entropies obtained from the density of states at the Fermi level showed that the electronic entropy of lithiation is quite small, however.

The configurational entropy from lithium-vacancy disorder was large enough to account for nearly all of the entropy of lithiation. This requires, however, that stoichiometric phases exist at the lithium concentrations of x=1/2 and x=5/6. The two-phase region between the semiconducting phase and the insulating phase therefore begins at a higher lithium composition than is usually given [3,4]. This phase boundary was consistent with the electrochemical measurements shown in figure 2. This figure also shows the three assessed contributions to the entropy of lithiation – electronic (el), phonon (ph), and configurational (cf). The composition range of the two-phase region between insulating and metallic Li_xCoO_2 is from x=0.83 to 0.93.

Figure 2 shows all contributions to the entropy of intercalation of Li into Li_xCoO_2. From the trends of these results, it is clear that the dominant contribution to the entropy of lithiation is the familiar entropy of mixing. The phonon and electronic terms are quite small in comparison.

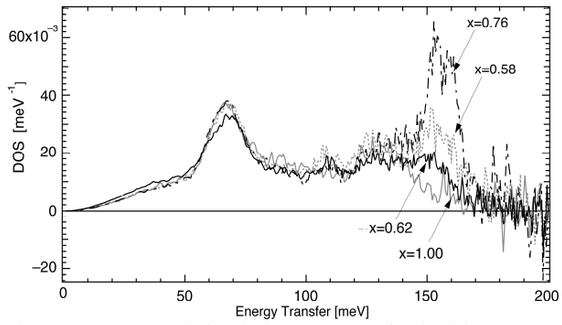

Fig. 1 Neutron-weighted DOS curves for incident energy of 243 meV. Labels "x" denote the Li concentration in Li_xCoO_2. DOS curves were normalized to unity up to 80 meV, ignoring OH/H_2O vibrational modes near 155 meV.

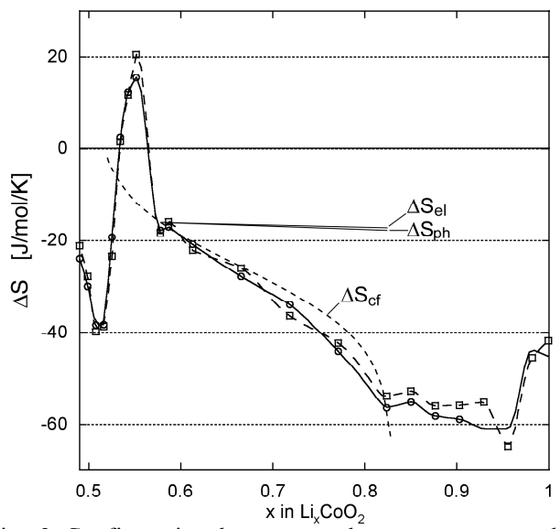

Fig. 2 Configurational entropy, phonon entropy, and electronic entropy contributions to the lithiation reaction in Li_xCoO_2 over the composition range $0.6 < x < 0.83$, superimposed on the electrochemical data from 2 cells.

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