

First-Principles Prediction of Vacancy Order-Disorder and Intercalation Battery Voltages in Li_xCoO_2

C. Wolverton and Alex Zunger

National Renewable Energy Laboratory, Golden, Colorado 80401

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We present a first-principles technique for predicting the ordered vacancy ground states, intercalation voltage profiles, and voltage-temperature phase diagrams of Li intercalation battery electrodes. Application to the Li_xCoO_2 system yields correctly the observed ordered vacancy phases. We further predict the existence of additional ordered phases, their thermodynamic stability ranges, and their intercalation voltages in $\text{Li}_x\text{CoO}_2\text{yLi}$ battery cells. Our calculations provide insight into the remarkable electronic stability of this system with respect to Li removal: A rehybridization of the Co-O orbitals acts to restore charge to the Co site ("self-regulating response"), thereby minimizing the effect of the perturbation. [S0031-9007(98)06670-8]

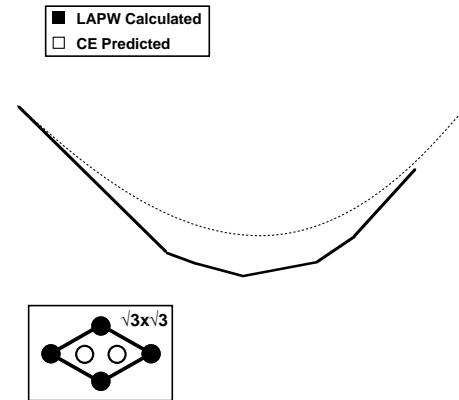
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In intercalation systems such as Li in graphite, hydrogen in metals, and alkali metals in transition-metal dichalcogenides [1], the "guest" atom occupies certain "host" sites preferentially at low temperatures while others remain empty. Because of this specificity of the interactions between the guest atoms and the intercalation lattice sites, a wide variety of intercalated structures

where f is a figure composed of several lattice sites (pairs, triplets, etc.) [9], D_f is the number of figures per lattice site, J_f is the Ising-like interaction for the figure f , and \overline{P}_f is a function defined as a product over the figure f of the variables S_i , averaged over all symmetry equivalent figures of lattice sites. We determine the effective interactions $\ln J_f$ for the intercalation ordering problem by fitting DH_{CESS}^d of N_s structures to LDA total energies DH_{LDASS}^d . The stability of the expansion was verified by removing structures from the fitting procedure and predicting their energies from the resulting expansion. The resulting CE is stable, has first-principles accuracy, and has predictive power to describe the energetics of any intercalation configuration in Li_xCoO_2 , even configurations of 100 000 atoms or more.

The *third step* of our approach involves subjecting the cluster expansion [Eq. (2)] to Monte Carlo simulations to ascertain both zero-temperature quantities (such as a prediction of the lowest-energy ordered vacancy phases) and finite-temperature properties (e.g., voltage profiles, order-disorder transitions, and the phase diagram associated with vacancy ordering). We use both canonical (fixed composition) and grand canonical (fixed chemical potential) simulations. System sizes of 8^3 – 32^3 – 512–32 768 sites were used with between 200–200 000 spin flips per site. For our zero-temperature study, we explored the lowest-energy structures among these 8^3 – 32^3 sites using a simulated annealing algorithm.

Predicted stable ordered vacancy compounds.—The lowest-energy stable ordered vacancy compounds predicted (out of the astronomical number of 2^N possible compounds) are shown in Fig. 1 as a function of Li content. Some of the predicted ground states are included in the original set of LDA-calculated energies (filled squares), but some are not (empty squares), and, hence, are truly unsuspected predictions. Our ground state calculations are in agreement with the observed ground state at $x \approx 1/2$: Reimers and Dahn [4] have observed electrochemically and through x-ray diffraction a monoclinic ordered vacancy compound at $x \approx 1/2$. Their data suggest a “2 3 1” two-dimensional ordering as we have predicted. The cluster expansion [Eq. (2)] also affords calculation of the energetics of configurations which are too complicated for direct LDA techniques, e.g., the energy of the random arrangement of Li and h units as a function of composition (Fig. 1). Also, we note that the cluster expansion constructed here is for a substitutional problem on a fixed lattice type (triangular planes with *ABC* stacking). However, it has been observed [10] and subsequently confirmed via first-principles energetics [11] that a shuffling of lattice planes occurs for low-Li content where the structure transforms in a nonsubstitutional manner to an *AAA*-type of stacking. We consider here only substitutional arrangements of Li and h for an *ABC* cation stacking, and, hence, do not account for possible vacancy ordered compounds which might occur on



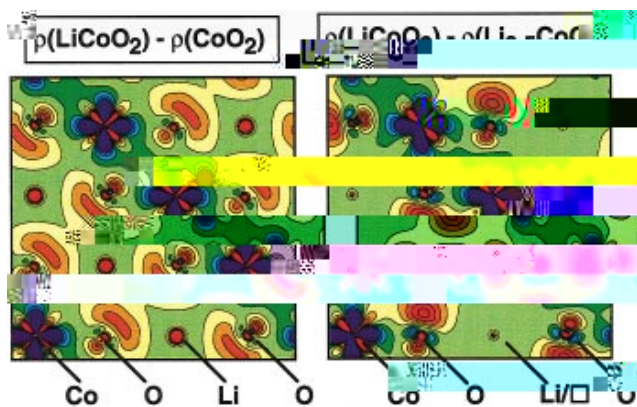


FIG. 2(color). Calculated charge density differences between LiCoO_2 , $\text{Li}_{0.5}\text{CoO}_2$, and hCoO_2 (all at the fixed, relaxed geometry of LiCoO_2) showing the change in Co-O hybridization upon Li removal (the self-regulating response). Red regions show the large positive charge density differences (charge density diminishes upon removal of Li) while blue regions indicate negative differences (charge density is enhanced upon Li removal).

the Co site. This “self-regulating response” [14,16] (minimizing the effect of external perturbations via rehybridization) is characteristic of systems having localized d states that communicate with a covalent manifold, e.g., transition-atom impurities in semiconductors [16]. It explains in such systems why the d -like energy levels do not shift significantly in response to large nominal changes in charge, and thus at least partly explains the defect tolerance of these structures over a large range of Li concentrations (Fig. 1).

First-principles prediction of $\text{Li}_x\text{CoO}_2/\text{Li}$ voltage profile.—For a $\text{Li}_x\text{CoO}_2/\text{Li}$ cell at temperature T , the voltage V_{cell} as a function of Li composition is given by [1,17] the Li chemical potential difference between cathode (Li_xCoO_2

