The Structure and Stability of the Layered $Li_xT_yM_{1-y}O_2$(T=Ni, Cr, Fe M=Co, Mn) system Using Molecular Dynamics

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Layered type cathode materials for the secondary lithium battery have been studied for a long time. Given the various possibilities of metastable structures that can be synthesized, a systematic study of the phase stabilities of the structure is very important. We performed Molecular Dynamics and the first principle calculations for an investigation of the electronic structures, and the stabilities of $LiMO_2$(M= Ni, Co, Mn) as well as $Li_xT_yM_{1-y}O_2$ (T=Ni, Cr, Fe M=Co, Mn) systems. The structures were built using fractional coordinates obtained from x-ray diffraction data. Electronic effect was observed with respect to the intercalation of lithium ion between the MO_2 layers. Energetics along the discharge of lithium ion also examined on each type of layered metal oxides. Projected density of states of the component atoms were analyzed.

On the other hand, molecular dynamic calculations have been carried out with the modified universal force field (MUFF) to investigate the phase transitions and properties of the $Li_xT_yM_{1-y}O_2$ (T=Ni, Cr, Fe M=Co, Mn) system. The minimized energies of the model systems could be used to predict the voltage through the relative scaling. These simple methods gave very good results for the structural changes including phase transitions of the models for the $Li_xNi_{1-y}Co_yO_2$ system.

Result and Discussions

For the comparison with the experimental voltage, first-principles calculations have been carried out for the Li_xNiO_2 models. The generalized gradient approximation by Perdew and Wang[1,2] was used. The average cell voltage V(x) can be easily calculated as

$$V(x) = -\frac{\Delta G_r}{F} \qquad (1)$$

where *F* is the Faraday constant and

$$\Delta G_r (= \Delta E_r + P\Delta V_r - T\Delta S_r) \quad (2)$$

ΔG_r is the Gibbs free energy for the reaction and can be approximated by the change in internal energy ΔE_r at 0 K. We calculated the cell voltage approximately using Eq. (1). If an effective calculation model is proposed, we will be able to estimate approximately the cell voltage for a model system from the minimization energies. We obtained the cell voltage of ca. 5.0 V from the minimization energies for the Li_xNiO_2 model. This result is not bad if it is considered that the experimental cell voltage is ca. 4.0 V.[3] First of all, the minimization energies show consistent tendency. If an appropriate scaling factor is used, we can obtain an effective cell voltage. Also, calculations using the CASTEP method[4] have been performed for the comparison. We obtained the cell voltage of ca. 4.3 V for the Li_xNiO_2 model with the CASTEP method. The present method using the MUFF and the method using first-principles calculations are thought to be complementary in their applications.

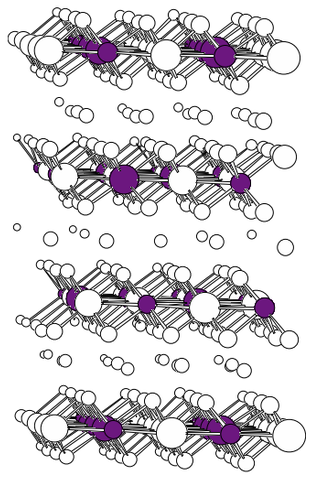

Figure 1. Optimized structure of the $Li_{0.4}Mn_{0.5}Ni_{0.5}$ using molecular dynamic calculations.

The $Li_xNi_{1-y}Co_yO_2$ system in the present work was only simple model of possible cathode materials in rechargeable secondary lithium batteries. Nevertheless, the theoretical study on this simple model proposed a useful method to reduce experimental labors. In the present work, potential parameters used in the MUFF were not fully optimized. Potential parameters for the composition of the MUFF would be adjustable to the experimental results or the results of first-principles calculations. As a result, we can optimize the potential parameters further to give a quantitative cell voltage profile. One of such optimizations will be a nonlinear combination of the potential parameters pertaining to oxidation states of +3 and +4.

Conclusions

A theoretical study for the structure and stability of the $Li_xNi_{1-y}Co_yO_2$ system as possible cathode materials in lithium secondary batteries has been performed. The structural changes according to the lithium intercalation in the $Li_xNi_{1-y}Co_yO_2$ have been simulated mainly using the minimization method with the modified universal force field. The cell voltage calculated from the minimization energies has been compared with the experimental cell voltage. The minimization energy of the $Li_xNi_{1-y}Co_yO_2$ system using the modified universal force field can be used to predict the cell voltage of the system through the relevant scaling. The mixed systems of transition metal, $Li_xT_yM_{1-y}O_2$ (T=Cr, Fe M=Co, Mn) did not show significant changes of the structures except some increment of cell volumes compare to the $Li_xNi_{1-y}Co_yO_2$.

References

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