

Mechanism of point defect formation in Na_xCoO_2 by first principle calculation with GGA+ U

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Na_xCoO_2 are known as p-type thermoelectric materials. They exhibit relatively high figure of merit, which is determined by three parameters, high Seebeck coefficient, high electronic conductivity and modest thermal conductivity. It is reported that high Seebeck coefficient is originated from a proper coexistence of Co^{3+} and Co^{4+} ions [1], while high electronic conductivity is a result of high concentration of electron holes [2]. As for the modest thermal conductivity, it is reported that Na vacancies are responsible for the decrease in the phonon thermal conductivity [3]. These three parameters are governed by the states of point defects including electronic defects. In order to improve the figure of merit or to search for new materials having higher figure of merit, it is necessary to obtain physical insight as to why and how those defects are present in this series of materials. These are the rationale for studying point defects by first principles calculations in this study.

In this study, we have examined the state of possible point defects by adding one point defect to a perfect state, with a variable x , since it is easily expected that interaction among many kinds of point defects present in this series of materials, whether intrinsic or extrinsic, is too complicated to acquire clear picture as to what is the influence of a defect on the system. Thus, we have calculated the formation energies of point defects by the first principle calculation using a GGA and GGA+ U (Hubbard U correction) methods [4]. The effective U values for the d orbital of Co atoms ranging from 0 to 10 eV with an increment of 1 eV were used. The structure obtained in the GGA approximation condition was used for GGA+ U calculations as well to reveal only the influence of the change in electric state by excluding modifications by the structure relaxation.

Within the wide range of the composition, or Na content, calculations were carried out for NaCoO_2 having no Na vacancy and $\text{Na}_{0.5}\text{CoO}_2$ in which half of Na sites are unoccupied. In order to minimize defect-defect interaction due to three periodic boundary conditions, supercells of which lengths are longer than 10 Å were used in this study. Plane wave cutoff energy, the number of k-points, and FFT mesh size were determined so that total energy was converged sufficiently enough within a several meV per atom.

Formation energy of a point defect, ΔE_f was calculated as

$$\Delta E_f = E_{\text{defective}}^{\text{total}} - E_{\text{perfect}}^{\text{total}} + n_M \mu_M + q(\varepsilon_F + E^{\text{correction}}) \quad (1)$$

where $E_{\text{defective}}^{\text{total}}$ and $E_{\text{perfect}}^{\text{total}}$ are the total energies of a defective supercell and a perfect supercell, respectively, n_M is the number of defects in the supercell, μ_M and is chemical potential of defective atoms, q is a charge state of the defective supercell, ε_F is fermi energy obtained for the perfect supercell, $E^{\text{correction}}$ is a correction term to cancel artificial energy shift due to introduction of jellium background charge to maintain charge neutrality of a defective supercell of non-zero charge state q .

The chemical potentials of constituting atoms were calculated by the following equations:

$$x\mu_{\text{Na}} + \mu_{\text{Co}} + 2\mu_{\text{O}} = \mu_{\text{Na}_x\text{CoO}_2}^{\text{total}} \quad (2) \quad \mu_{\text{Na}} : \mu_{\text{Co}} = \mu_{\text{Na}_2\text{O}}^{\text{Na}_2\text{O}} : \mu_{\text{Co}_3\text{O}_4}^{\text{Co}_3\text{O}_4} \quad (3)$$

$$\mu_{\text{Na}_2\text{O}}^{\text{Na}_2\text{O}} = (\mu_{\text{Na}_2\text{O}}^{\text{total}} - \mu_{\text{O}}) / 2 \quad (4) \quad \mu_{\text{Co}_3\text{O}_4}^{\text{Co}_3\text{O}_4} = (\mu_{\text{Co}_3\text{O}_4}^{\text{total}} - 4\mu_{\text{O}}) / 3 \quad (5)$$

where $\mu_{\text{Na}_x\text{CoO}_2}^{\text{total}}$, $\mu_{\text{Na}_2\text{O}}^{\text{total}}$ and $\mu_{\text{Co}_3\text{O}_4}^{\text{total}}$ are the total energies per unit formula of the each bulk

material and are constant. Then, μ_{Na} , μ_{Co} , μ_{Na_2O} and $\mu_{Co_3O_4}$ can be calculated as a function of chemical potential of O which can be calculated from

$$\mu_O = \mu_O^0 + k_B T \ln(P_O / P_O^0) \quad (6)$$

where P_O is partial pressure of oxygen gas and P_O^0 is that at standard state, fixed at 0.2 atm, and k_B and T is Boltzmann constant and temperature, respectively. The value of μ_O^0 was assumed to be equal to energy per atom of O_2 molecule at 0 K, which was also calculated independently.

When the electronic correlation was introduced, the electrostatic potential of Co in $Na_{0.5}CoO_2$ was divided into two groups, which means that the on-site Coulombic interaction is responsible for disproportionation of cobalt charges. Figure 1 shows the calculated formation energies of defects in $Na_{0.5}CoO_2$ with GGA and GGA+ U ($U = 5.0$ eV). In the case of GGA, Co^{4+} vacancy had the lowest formation energy in $Na_{0.5}CoO_2$. However, the formation of Co vacancy is unlikely because of following reasons. Firstly, an O vacancy had relatively high formation energy. It means that it is difficult to precipitate metal oxides within a sample except for the surface region of the sample. Secondly, the chemical potentials of a Co atom of Co gas, 9.43 eV, were extremely high compared with the one of Na atom of Na gas, 0.81 eV. When the electronic correlation was introduced, the formation energy of Co vacancy increased. In other words, the electronic correlation makes CoO_2 layer stable. On the other hand, the formation energy of a Na vacancy exhibited relatively low value. Furthermore, the energy of Na atom insertion showed very low and negative value. They indicate that Na atom can be inserted than other atoms. It confirms that the experimental fact that only Na content is easily changeable at ordinary environment [5].

References

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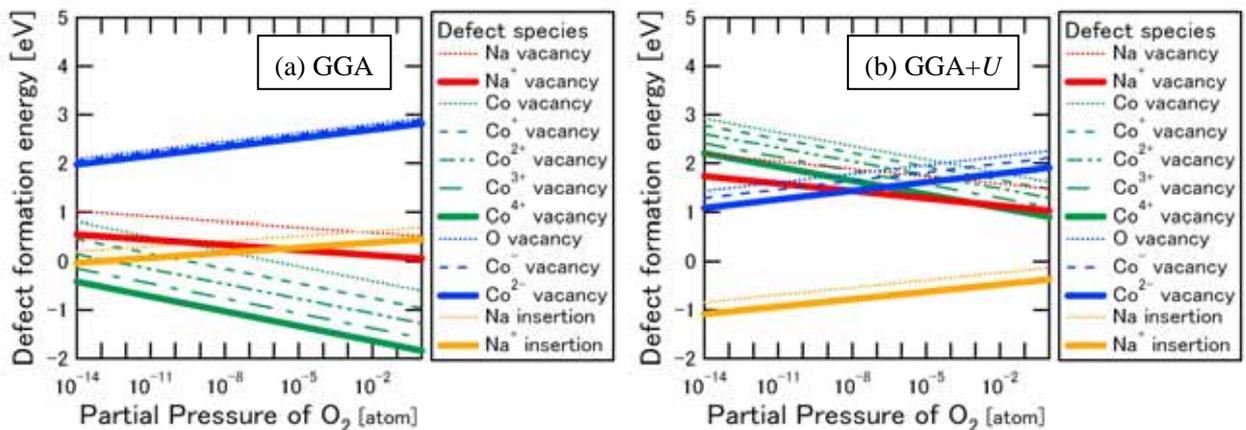


FIG. 1 Formation energies of various charge states of defects in $Na_{0.5}CoO_2$ as a function of oxygen partial pressure with (a) GGA and (b) GGA+ U ($U = 5.0$ eV).