

### First-principles study on doping and defect chemistry in LiCoO<sub>2</sub>

Yukinori Koyama,<sup>1</sup> Hajime Arai,<sup>1</sup> Isao Tanaka,<sup>2</sup>  
Yoshiharu Uchimoto,<sup>3</sup> Zempachi Ogumi<sup>1</sup>

<sup>1</sup> Office of Society-Academia Collaboration for Innovation, Kyoto University, Uji, Kyoto 611-0011, Japan

<sup>2</sup> Graduate School of Engineering, Kyoto University, Sakyo, Kyoto 606-8501, Japan

<sup>3</sup> Graduate School of Human and Environment Studies, Kyoto University, Sakyo, Kyoto 606-8501, Japan

#### Introduction

Lithium transition-metal oxides are used as electrode active materials for lithium-ion batteries. To improve battery performance, doping to active materials is often carried out. The doped ions can be considered as extrinsic point defects, and the doping may have an influence on native defects in the active materials. Since the point defects are associated with many properties of the materials, information on the doped ions as well as the native defects is of importance for understanding the characteristics of the electrode active materials.

We have reported theoretical study on the native defects in layered lithium transition-metal oxides such as LiCoO<sub>2</sub> and LiNiO<sub>2</sub> using first-principles calculations based on density functional theory (DFT) [1]. In this study, we extend this approach to doping as extrinsic defects, and we report estimation of solubility limit of the doped ions in LiCoO<sub>2</sub> and effects of the doping on defect chemistry.

#### Calculation method

As the doped ions to LiCoO<sub>2</sub>, several metals including Na, Mg, Al, Zr and Nb were examined. Both the Li and Co sites were considered as substitution positions of the doped ions. Vacancies, interstitial cations and antisite defects were considered as the native defects.

Equilibrium defect concentrations were estimated by the Boltzmann distribution under given chemical conditions and charge neutrality. Defect formation energy was calculated by first-principles calculations using a supercell consisting of 144 atoms with a single defect. The first-principles calculations were carried out using the plain-wave basis PAW method and the GGA+U exchange correlation functional.

#### Results and discussion

Figure 1(a) illustrates equilibrium defect concentrations of the native defects in undoped LiCoO<sub>2</sub> at oxygen partial pressure of 0.2 atm and the Li-rich condition (coexisting with Li<sub>2</sub>O) as a function of temperature. Antisite Co ion at the Li site (Co<sub>Li</sub>) is the dominant defect in LiCoO<sub>2</sub>. At usual synthesis conditions of LiCoO<sub>2</sub> (800–900 °C in air), the equilibrium concentration of Co<sub>Li</sub> is 1% or less. It is, therefore, expected that LiCoO<sub>2</sub> with low defect concentrations is easily synthesized.

As Al forms complex oxides with Li, e.g. Li<sub>5</sub>AlO<sub>4</sub> and LiAlO<sub>2</sub>, maximization of Al doping (maximum Al chemical potential) and minimization of Li deficiency (maximum Li chemical potential) are incompatible. Therefore, defect concentrations are estimated at typical chemical conditions, where LiCoO<sub>2</sub> coexists with two other Li–Al oxides. Figure 1(b) illustrates equilibrium defect concentrations when LiCoO<sub>2</sub> coexists with Li<sub>2</sub>O and Li<sub>5</sub>AlO<sub>4</sub>. This condition corresponds to the maximum Li chemical potential. Al ions preferentially occupy the Co site (Al<sub>Co</sub>) in LiCoO<sub>2</sub>, and the equilibrium concentration is estimated to be ~5%. Because of the Li-rich condi-

tion, excess Li reacts with Al, resulting in suppression of the Al doping to LiCoO<sub>2</sub>. As Al is trivalent, the Al substitution for the Co site has no effect upon the defect concentrations of the native defects.

For higher Al chemical potential, a condition where LiCoO<sub>2</sub> coexists with Li<sub>5</sub>AlO<sub>4</sub> and LiAlO<sub>2</sub> is examined. The equilibrium concentration of Co<sub>Al</sub> is ~50% at this condition, as shown in Fig. 1(c). Although the higher Al chemical potential results in lower Li chemical potential, increase of other defects is not significant. When LiCoO<sub>2</sub> coexists with LiAlO<sub>2</sub> and LiAl<sub>5</sub>O<sub>8</sub> with much higher Al chemical potential, i.e. much lower Li chemical potential, concentrations of Co<sub>Li</sub> and interstitial Co ion (Co<sub>i</sub>) are almost 100%. Such extremely high defect concentrations suggest that LiCoO<sub>2</sub> is no longer stable at the high Al chemical potential; excess Al reacts with Li in LiCoO<sub>2</sub>.

These results indicate that consideration of the chemical condition, i.e. chemical potentials of Li and doped ion, is of importance to obtain high concentration of the doped ion without increase of other defects. The doping will be compared among the different metals and factors affecting the solubility limit will be discussed at the meeting.

#### Acknowledgement

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#### References

[1] Y. Koyama, H. Arai, I. Tanaka, Y. Uchimoto, Z. Ogumi, *Chem. Mater.*, 24 (2012) 3886.

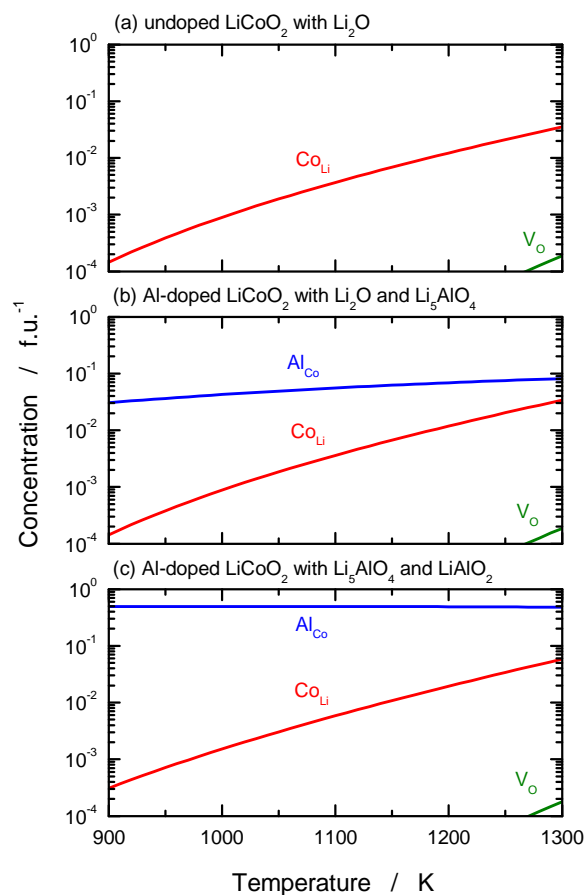


Figure 1 Equilibrium concentrations of the point defects in (a) undoped LiCoO<sub>2</sub> coexisting with Li<sub>2</sub>O, (b) Al-doped LiCoO<sub>2</sub> coexisting with Li<sub>2</sub>O and Li<sub>5</sub>AlO<sub>4</sub>, and (c) Al-doped LiCoO<sub>2</sub> coexisting with Li<sub>5</sub>AlO<sub>4</sub> and LiAlO<sub>2</sub>.