

Comparison of Phase Stability in Layered NaCrO₂ and LiCrO₂ Oxides by First-principles DFT Calculations
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Introduction

Application for large-scale energy storage device such as lithium ion batteries has been investigated. However, an alternative to lithium ion batteries should be required due to the cost and geopolitical limit of lithium sources. Recently sodium ion batteries have recently attracted considerable attention as energy storage device alternative to lithium ion batteries, since sodium source is abundant and low cost. Although layered LiCrO₂ is electrochemically inactive, layered NaCrO₂ shows electrochemically active with good cycling properties [1]. Therefore layered NaCrO₂ is one of the promising cathode materials for sodium ion batteries. The phase transition from O3-type with octahedral NaO₆ site to P3-type structure with prismatic NaO₆ site takes place at around $x = 0.4$ in Na_{1-x}CrO₂ ($0 \leq x \leq 1$) during sodium de-intercalation process [2]. In this work, phase stability between O3-type and P3-type structure in layered NaCrO₂ and LiCrO₂ is compared by using first-principles DFT calculations and difference of electrochemical properties between them are discussed.

Method

The Vienna ab initio simulation package (VASP) was utilised with the generalised gradient approximation (GGA-PBE) + U and projector-augmented wave (PAW) methods. For the GGA + U calculations, the U values for the d-orbitals of Cr were set to 3.5 eV following relevant previous reports. Defect formation energy derived from Cr defect at the interstitial site was calculated for both O3-type and P3-type structure of NaCrO₂ and LiCrO₂ by first-principles DFT calculations.

Results and Discussion

Evaluation of phase stability between O3-type and P3-type structure for NaCrO₂ and LiCrO₂ is conducted. Using fully intercalated ($x = 0$) and de-intercalated ($x = 1$) composition as the reference states, formation energies of intermediate state, defined by following equation, was calculated by first-principles calculations.

$$\Delta E_f(A_{1-x}CrO_2) = E(A_{1-x}CrO_2) - xE(CrO_2) - (1-x)E(ACrO_2) \quad (1)$$

As shown in Fig. 2, O3-type structure is more stable than P3-type structure for Li_{1-x}CrO₂ in $0 \leq x < 1$ region. This finding agrees with experimental report [3]. On the other hand, O3-type structure is more stable than P3-type structure for Na_{1-x}CrO₂ in $0 \leq x \leq 0.4$ region, which agrees with experimental report [2]. In $0.4 \leq x$ region, formation energies for O3 type and P3-type structure shows similar values at 0 K, suggesting that P3-type structure can be stable phase at ambient temperature, which is consistent with experimental report [2].

Defect formation energy derived from Cr defect at the interstitial site was calculated for O3-type and P3-type structure of NaCrO₂ and LiCrO₂ by first-principles

calculations. Table 1 shows corresponding defect formation energy with the nearest neighbour alkali-ion vacancies from Cr defect. When the three nearest neighbour alkali-ions from Cr defect are de-intercalated, defect formation energies are 2.817 eV for O3-type NaCrO₂ and 0.401 eV for O3-type LiCrO₂. It is found that NaCrO₂ is hard to form Cr defect compare to LiCrO₂. Furthermore, defect formation energy decreases with increase the number of de-intercalated Li ions in O3-type LiCrO₂. Thus, Cr migration into alkali layer can take place during the Li de-intercalation process, which results in capacity fading during the charge-discharge cycling. This finding is consistent with the discussion by Komaba et al., it could explain that NaCrO₂ shows higher charge and discharge capacity than LiCrO₂.

References

- [1] S. Komaba, C. Takei, T. Nakayama, A. Ogata, N. Yabuuchi, *Electrochem. Comm.*, **12** (2010) 355-358.
- [2] S. Komaba, T. Nakayama, A. Ogata, T. Shimizu, C. Takei, S. Takada, A. Hokura, I. Nakai, *ECS Transactions*, **16** (2009) 43-55.
- [3] S.-T. Myung, S. Komaba, N. Hirosaki, N. Kumagai, K. Arai, R. Kodama, I. Nakai, *J. Electrochem. Soc.*, **150** (2003) A1560-A1568.

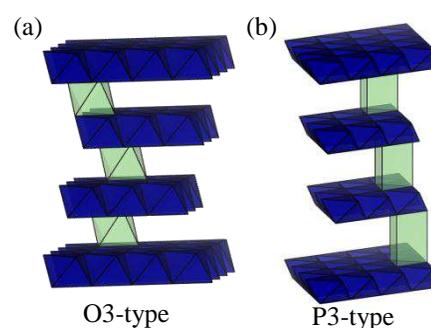


Fig. 1. Crystal structure of (a) O3-type and (b) P3-type ACrO₂ (A = Li, Na).

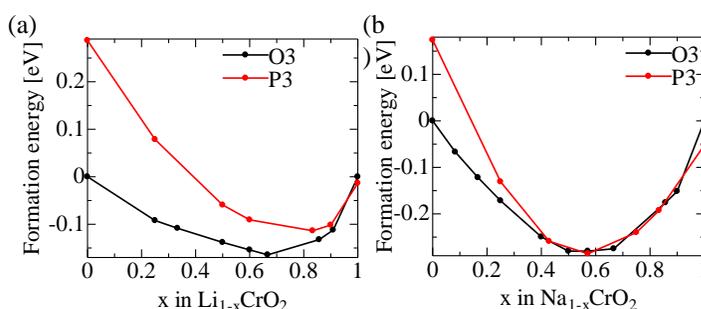


Fig.2. The formation energies for the most stable A/vacancy arrangement at each compositions (x) of the O3 and P3 type of (a) LiCrO₂ and (b) NaCrO₂ calculated by ab initio DFT.

Table 1. Defect formation energy derived from Cr penetration into alkali layer for the O3 and P3 type of LiCrO₂ and NaCrO₂.

		Number of de-intercalated alkali-ions			
		0	1	2	3
O3	LiCrO ₂	N/A	2.490	1.323	0.401
	NaCrO ₂	N/A	N/A	2.825	2.817
P3	LiCrO ₂	4.870	1.916	-2.608	-2.926
	NaCrO ₂	N/A	N/A	3.879	3.113