

# Electrode potential and activation energy of sodium transition-metal oxides as cathode materials for sodium batteries: A first-principles investigation



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## ABSTRACT

Recently, researches on sodium (Na) batteries get resurrected for large-scale applications under the background of limited lithium (Li) resource. Four layered sodium transition-metal (TM) oxides, NaMO<sub>2</sub> (M = V, Cr, Co and Ni) with  $\alpha$ -NaFeO<sub>2</sub> type as potential cathode materials for sodium batteries, are systematically investigated by first-principles calculations. As two key properties for a successful cathode material, the electrode potential and activation energy ( $E_A$ ) of Na<sup>+</sup> in their parent NaMO<sub>2</sub> crystals (M = V, Cr, Co and Ni) are reported. Our results suggest that NaCrO<sub>2</sub>, NaCoO<sub>2</sub> and NaNiO<sub>2</sub> possess satisfying average electrode potential (AEP) and their potential platforms are close to that of LiCoO<sub>2</sub> to a large extent. Meanwhile,  $E_A$  of these materials are all acceptable for batteries. These first-principles results suggest that layered NaCrO<sub>2</sub>, NaCoO<sub>2</sub> and NaNiO<sub>2</sub> are viable candidates for large-scale applications.

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## 1. Introduction

A battery is about storing a certain amount of energy used as a temporary power supply. At the beginning of 19th century, many kinds of primary batteries arose one after another, but their materials are commonly toxic and they can be used for only once. Later, invention of rechargeable batteries improved material's use factor and contributed to the environmental protection. When stepping into current century, human are confronting carbon pollution that causes climate change, resulting from long term accumulation of reckless burning fossil fuel. Among that, about a quarter of emissions come from transportation. Thus, developing battery technology has been vested with new meaning – a way to reduce greenhouse gas by large-scale stationary energy storage. For instance, the usage of fossil fuel can be reduced through revamping transportation sector gradually with the battery technology for auxiliary power units in electric vehicles (EVs) [1] and storing intermittent energy generated by wind and solar for the grid [2,3].

At present, Li-ion batteries (LIBs) [4–6], especially those utilizing LiCoO<sub>2</sub> cathode with high efficiency, have distinguished themselves in the area of portable electronic devices [7,8], and they can be also used in large scale applications for reduction of the exhausted CO<sub>2</sub>. However, there is a rising concern about the source of lithium salts for LIBs considering the rocketing consumption of its portable products nowadays, particular for the larger scale applications [9]. Indeed, both Na-ion and Li-ion electrodes were investigated in tandem during the 1970s–1980s, but LIBs have been received much more attentions for their relatively better performance. Recently, research interest in Na-ion batteries (NIBs) arouses wide attention again [10–12], owing to at least three reasons. Firstly, Na is an element of far more abundance in the earth crust and with lower toxicity than Li. Secondly, since the chemistry of Na is close to Li, those chemical approaches used in development of LIBs can provide a good reference to develop NIBs. Similar or better performance is able to be available in many cases compared to Li ion analogue [13–17]. Thirdly, for the large-scale battery applications, the major concern is not the high energy density but the lower projected cost of raw materials for manufacturing and electrode recycling [18].

Due to the successful application of LiCoO<sub>2</sub>, layered NaMO<sub>2</sub> (M = Co, Cr, Ni and V) has hold great hope, and their performance of electrode potential and reversible capacity have been intensively

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investigated. Komaba et al. revisited  $\text{NaCrO}_2$  electrode with currently available equipments and found that the highly reversible capacity was 104 mAh/g in case of cutoff voltage at 3.6 V, and that the extraction of  $\text{Na}^+$  per mole of  $\text{NaCrO}_2$  can be up to 0.5 mol [19], whereas it was only 0.15 mol in earlier report [20]. Moreover, improved discharge capacity remained 110 mAh/g after 40 cycles in carbon-coated  $\text{NaCrO}_2$  cathode [21]. Similar to the case of  $\text{NaCrO}_2$ , at least 0.5 mol  $\text{Na}^+$  can be reversibly electrochemically deintercalated from  $\text{NaVO}_2$  which corresponds to a capacity of 126.4 mAh/g [22]. Vassilaras et al. reported the  $\text{NaNiO}_2$  cell has 123 mAh/g discharge capacity when cycling at 1.25–3.75 V over 20 cycles with no significant structural change and minor capacity fade [23]. Satisfying cycle performance was also demonstrated in a variety of Na cobalt bronze phases by Shacklette et al. [24]. All these results imply that layered  $\text{NaMO}_2$  are glamorous contenders for NIBs. Thus, comprehensive understanding on their electrochemical behaviors is imperative.

Note that the currently available studies on NIBs mainly focus on the experimental side [21–32], whereas theoretical and computational studies remain relatively sporadic [33–35]. Here we systematically investigate the electrochemical properties of the layered  $\text{NaMO}_2$  ( $M = \text{Co}, \text{Cr}, \text{Ni}$  and  $\text{V}$ ) as potential cathode materials for Na batteries using first-principles method, which is a powerful tool to unveil the microscopic mechanism of various functional materials [36]. Though electrode potential and diffusion barrier are two fundamental properties for a battery, the detailed variation of electrode potentials in  $\text{Na}_x\text{MO}_2$  with Na content ( $0 \leq x \leq 1$ ) and activation energy ( $E_A$ ) of  $\text{Na}^+$  in them, to our knowledge, have not been explored computationally yet. Therefore, here we aim to address the following critical issues: (1) What are their electrochemical performance and characteristics with variation of Na-content? (2) How about their  $E_A$ ? (3) What is the role of different TM elements in the battery performance?

## 2. Structural models and computational methods

In this work, our supercell models of  $\text{NaMO}_2$  crystal for computing average electrode potential (AEP) and  $E_A$  were generated from  $3 \times 3 \times 1$  and  $2 \times 2 \times 1$  unit cell, respectively, which are all O3 type structures with  $R\bar{3}m$  space group (ABCABC oxygen stacking,  $\text{Na}^+$  in the octahedral site) [37]. As an example, the unit cell of  $\text{NaCoO}_2$  is shown in Fig. 1. *Ab initio* calculations were performed using the density functional theory (DFT) with the Perdew–Burke–Ernzerhof (PBE) [38] functional within generalized gradient approximation and the projector-augmented wave (PAW) [39] method as implemented in the Vienna *ab initio* simulation package (VASP) [40,41]. GGA + U method was not adopted because it would only result in a systematic shift of the theoretical values, but scarcely affect the variation trend with the different Na systems. Besides, GGA is a better approximation than GGA + U for the analysis of Na intercalation voltage,  $c$  parameter and ground states in the composition range  $0.5 \leq x \leq 0.8$  of  $\text{Na}_x\text{CoO}_2$  [34]. The wave functions were expanded in plane waves up to 400 eV cutoff, and the Brillouin zone  $\mathbf{k}$  point grids were  $3 \times 3 \times 2$  and  $4 \times 4 \times 2$  Monkhorst–Pack  $\mathbf{k}$  grids, depending on the supercell size for computing AEP and  $E_A$ , respectively. Our test calculations show that further increasing cutoff energy or  $\mathbf{k}$  grid only leads to little changes on the computational results.

To compute AEP for  $\text{NaMO}_2$ , every time three Na ions were removed randomly from the supercell model, which corresponds to a charging process. Similar computational method has been employed to simulate electrode potentials in LIBs [42]. We used the climbing-image nudged elastic band (CI-NEB) method [43] with minimization of a set of intermediate images for Na diffusion to search saddle points along the minimal energy pathway (MEP).

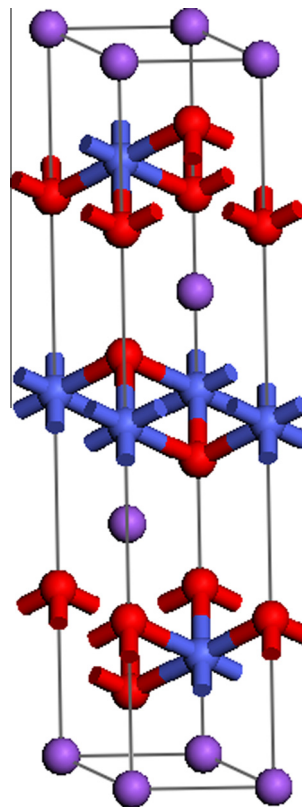


Fig. 1. Crystal structure of the layered  $\text{NaCoO}_2$  crystal. Oxygen: red, cobalt: blue, sodium: purple. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The lattice parameters were fully fixed with convergence criteria of the force on each atom less than 0.02 eV/Å. Different from those obtained in the lithium intercalation, the spin polarization effect is not negligible for these  $\text{NaMO}_2$  oxides [44]. Hence, spin polarization was included during our DFT calculations.

## 3. Results and discussion

### 3.1. Electrode potentials

The lattice parameters ( $a$  and  $c$ ) for  $\text{NaMO}_2$  crystals of O3 type from present calculations are shown in Table 1, along with previous experimental data and DFT results [19,44–49]. Our calculations are basically in agreement with the experimental results, with a deviation less than 3%. This indicates that our computational

Table 1  
Lattice parameters ( $a$ ,  $c$ ) for  $\text{NaCoO}_2$ ,  $\text{NaCrO}_2$ ,  $\text{NaNiO}_2$ , and  $\text{NaVO}_2$  crystals.

	Methods	$\text{LiCoO}_2$	$\text{NaCoO}_2$	$\text{NaCrO}_2$	$\text{NaNiO}_2$	$\text{NaVO}_2$
$a$ (Å)	This work	2.828	2.899	2.987	2.957	2.961
	DFT	2.833 <sup>a</sup>	2.86 <sup>c</sup>	–	2.89 <sup>e</sup>	–
	Expt.	2.814 <sup>b</sup>	2.890 <sup>d</sup>	2.976 <sup>e</sup>	2.960 <sup>f</sup>	2.998 <sup>g</sup>
$c$ (Å)	This work	13.804	15.208	15.628	15.314	15.972
	DFT	13.817 <sup>a</sup>	14.90 <sup>c</sup>	–	15.20 <sup>e</sup>	–
	Expt.	14.044 <sup>b</sup>	15.609 <sup>d</sup>	15.964 <sup>e</sup>	15.759 <sup>f</sup>	16.106 <sup>g</sup>

<sup>a</sup> Ref. [49].

<sup>b</sup> Ref. [48].

<sup>c</sup> Ref. [44].

<sup>d</sup> Ref. [45].

<sup>e</sup> Ref. [19].

<sup>f</sup> Ref. [46].

<sup>g</sup> Ref. [47].

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