

First-Principles Study of Na ion Diffusion in NaCoPO₄: Positive Electrode Material for Rechargeable Sodium ion Batteries

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ABSTRACT: The diffusion mechanism of Na ions in the orthorhombic group olivine-type NaCoPO₄ is investigated by first-principles DFT (Density Functional Theory) calculations. The energy barriers for possible spatial hopping pathways are calculated with the adiabatic trajectory method. The calculations show that the energy barriers running along the *c* axis are about 0.68, 1.29, and 1.415 eV for NaCoPO₄, CoPO₄, and Na_{0.5}CoPO₄, respectively. Conversely, the other migration pathways have much higher energy barriers resulting in very low probability of Na-ion migration. This means that the diffusion in NaCoPO₄ is one dimensional. The one-dimensional diffusion behavior has also been shown with full *ab initio* molecular dynamics simulation, through which the diffusion behavior is directly observed.

KEYWORDS: First-principles calculations, Density functional theory, Na-ion batteries, Na ion diffusion, GGA+U Optimization, olivine-type NaCoPO₄.

I. INTRODUCTION

Today Li-ion batteries are playing a vital role in energy storage systems since they have high energy density [1,2]. On the other hand they are facing some problems in large-scale grid storage systems because they are limited due to the high cost, low abundance of Li metal and organic electrolytes [3]. After that to Li, Na is second metallic element having lower ionic radius (0.97 Å) and similar intercalating properties of Li. Consequently in order to decrease the cost and improve the safety, using both Na-based intercalating materials and aqueous electrolyte used is one of the recent strategies instead of Li based materials [3,4]. First principle methods is a useful tool for identifying materials for developing Na-ion batteries. In this regard, various sodium based electrode materials including NaFePO₄, NaMnPO₄, Na₄Mn₉O₁₈, Na_xMnO₂, NaVPO₄F have been experienced as electrode materials for energy storage applications due to its Na-ion intercalating properties, low cost and environmental friendliness.

In this paper, we are successfully demonstrating olivine-type NaCoPO₄ cathode material for Na-ion batteries. Present study we take Olivine-type NaCoPO₄ (ICSD# 82752) for Na ion migration and energy optimization. NaCoPO₄ has an orthorhombic structure with Pnma space group and 28 atoms are used to energy optimization. Since the chemical diffusion coefficient is sensitive to the Na content in the Na_δCoPO₄ material, three typical Na concentrations are thus calculated: $\delta = 1, 0.5, \text{ and } 0$. For each Na concentration, the ionic positions, lattice parameters and cell volume are relaxed with the conjugate gradient method using forces and stresses.

II. COMPUTATIONAL METHOD

The First principle calculations have been performed using the Quantum ESPRESSO PWscf code [5] using a plane-wave basis to express the wave function of the valence electrons and ultrasoft pseudopotentials to describe the

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interactions of ionic cores and valence electrons [6]. QuantumWise VNL-ATK 2016 academic version was used as GUI for Quantum ESPRESSO. The exchange-correlation contribution was described by the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof [7]. Onsite Coulomb correction (GGA + U) was included to describe the localized electronic states of Co 3d in mixed-valence rare earth metals. A spin polarization calculation was used. A kinetic cutoff energy of 520 eV, and $5 \times 5 \times 3$ k-point meshes in the NaCoPO₄ unit cell (28 atoms) were found by a convergence test ($< 3\text{meV/NaCoPO}_4$). Because the band gaps of both compounds were underestimated, this is typical of the GGA + U functional [8]. The relaxation of unit cell volume was done by total-energy minimization, and atom positions were relaxed until the remaining force acting on the atoms was less than 10^{-3} eV/Å. The Na diffusion in NaCoPO₄ is calculated by Na jumps between neighboring Co sites were obtained by means of the nudged elastic band (NEB) method [9]. The threshold for the total force that is acting on the NEB images of the interpolated reaction path was set to 0.05 eV/Å. Arrhenius plot is obtained calculating reaction rates using the nudged elastic band (NEB) method and harmonic transition state theory (HTST) [10].

III. RESULTS AND DISCUSSION

Fig. 1 Shows the bulk crystal structure of sodium Cobalt phosphate [NaCoPO₄] in different projection direction. The olivine structure of the NaCoPO₄ (Fig. 1 a) is a hexagonal close-packed array of oxide ions containing isolated PO₄ tetrahedral and corner-sharing CoO₆ octahedral in the (0 1 1) plane and edge-sharing NaO₆ octahedral, stacked along the (0 1 0) direction. Because the oxygen atoms are strongly bonded to both Co and P atoms.

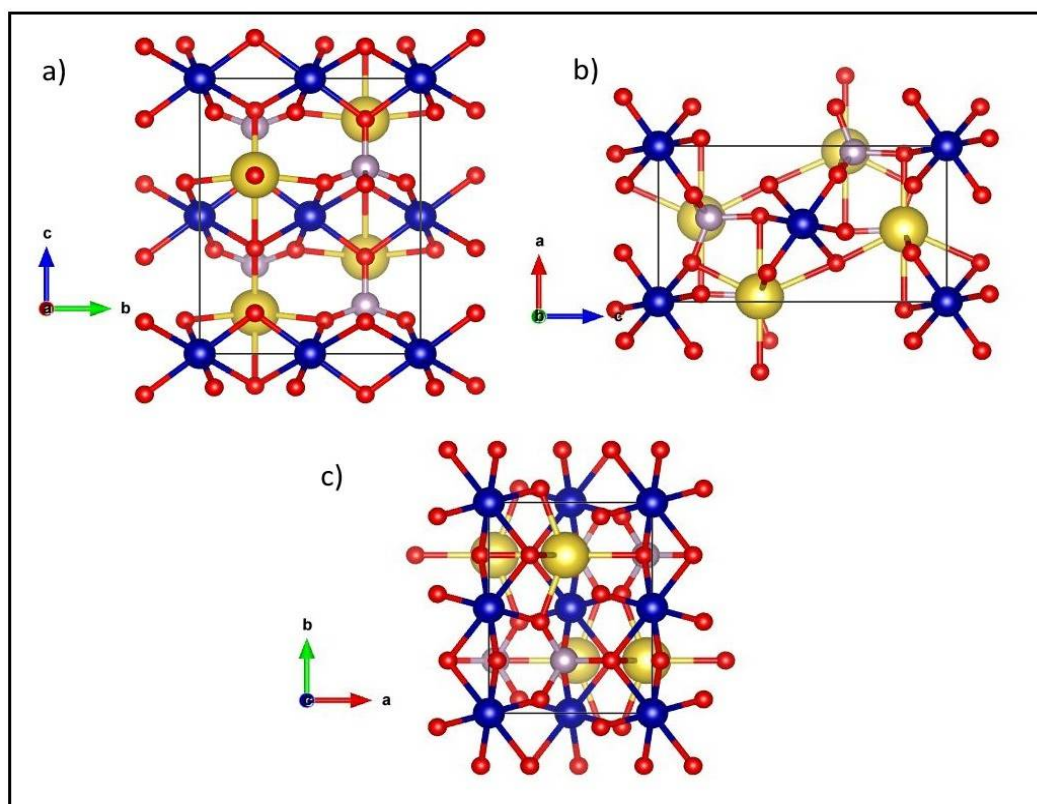


Fig. 1 Crystallographic structure of the bulk NaCoPO₄ a. (0 1 1) b. (1 0 1) c. (1 1 0) directions (Yellow, red, violet and blue balls refer to Na, O, P and Co atoms, respectively).

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Table 1. Optimized lattice constants for olivine-type Na_8CoPO_4 (Å)

Na_8CoPO_4		a Å	b Å	c Å	Corrected Energy
Experimental		5.069	6.877	8.974	-181.1891 eV
$\delta=1$	Computed	5.080	6.870	8.975	-199.9217 eV
$\delta=0$	Computed	5.089	6.701	8.890	-174.1243 eV
$\delta=0.5$	Computed	5.084	6.804	8.924	-179.3212 eV

Table I summarizes the optimized structure after the ionic relaxation with conjugate gradient method. It can be seen that the lowest total energy obtained at $\delta=1$, and highest achieved at $\delta=0$, this indicating a most favorable configuration and will be chosen as the objective of the following calculations for the case of NaCoPO_4 . Fig. 2 shows the partial density of states (PDOS) around the Fermi level for olivine-type NaCoPO_4 , at $\delta=1$. The localized Co 3d bands form a valence band maximum and conduction band minimum, and the band gaps are larger than 2.692 eV in NaCoPO_4 . Therefore, the intrinsic band conduction of electrons is negligible at room temperature because of the localization and wide band gap. Electronic conduction in NaCoPO_4 mainly arises from localized electron/hole (polaron) hopping [11]. Polarons are created by the redox reaction of $\text{Co}^{2+/3+}$ to maintain charge neutrality during electrochemical Na^+ removal (uptake). In Fig. 2 the calculated energy profiles for localized hole (Co^{3+}) jumps of ~ 0.3 eV for both compounds. The polaron migration energies are much smaller than the band gaps, and thus polaron migration is the dominant electron conduction mechanism. The similarity of the polaron migration energies of the two compounds indicates that the difference in rate performance does not stem from polaronic migration. Alkali ion migration is another factor affecting the rate performance in batteries.

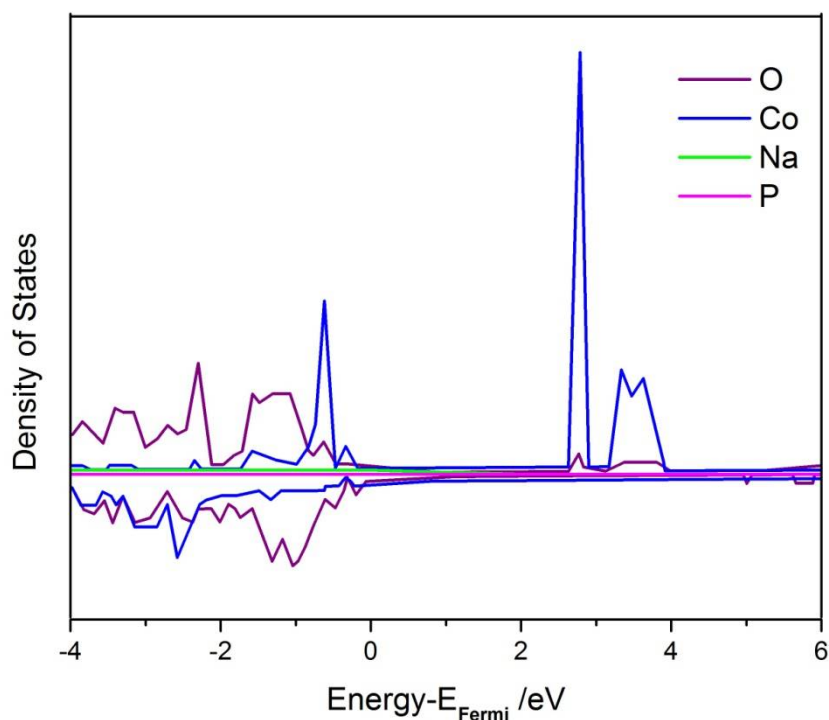


Fig. 2 Partial density of states (PDOS) for NaCoPO_4 (PDOS is aligned so that the Fermi energy is zero)

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It seems that diffusion pathways is always crucial in understanding the microscopic diffusion mechanism. In order to calculate the diffusion pathways for the Na ions, we have employed the ‘‘adiabatic trajectory method’’ [12, 13] after the structural optimization. In this method, one chosen Na ion is pushed to move with a small, constant speed in a given direction, and all other atoms are relaxed continuously in response to the Na ion motion. The energy barrier can be obtained conveniently through monitoring the changes of the total energy. This method has been found to be a viable alternative to a costly point-by-point determination of the potential energy surface.

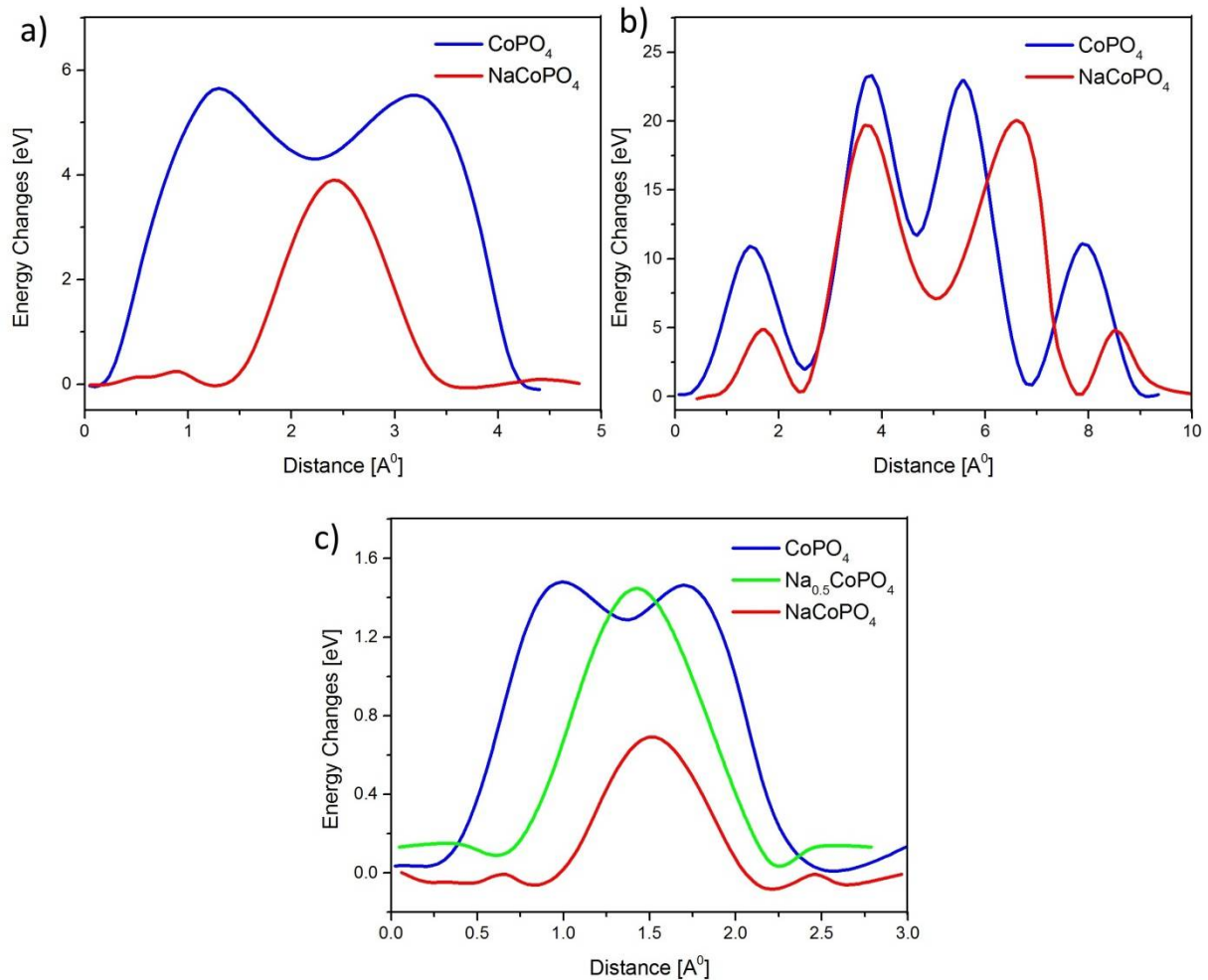


Fig. 3 Energy barriers of three different diffusion pathways (a-c) are for the migrating direction running along the *a*, *b*, and *c* axis, respectively.

Fig. 3c shows that the energy barriers along the *c* direction is about 0.68, 1.29 and 1.415 eV for NaCoPO_4 , CoPO_4 , and $\text{Na}_{0.5}\text{CoPO}_4$ respectively. The different energy barriers for the three species are mainly due to the different atomic surroundings of the diffusion pathway, including the different ionic position and bonding length (lattice vector), which is the direct result of the different Na concentration. However, the energy barriers along the other two directions are much higher that prohibits the diffusion occurs along these two directions, as shown in Fig. 2a and 2b. This means that

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the diffusion in NaCoPO_4 is one dimensional. As the energy barrier along c direction for NaCoPO_4 is lower than that of CoPO_4 , and $\text{Na}_{0.5}\text{CoPO}_4$, the diffusion coefficient will be higher, which is consistent with Prosini's experimental results. However, the energy barrier along c axis direction is also much higher than that of a -axis direction. The conclusion of the one-dimensional diffusion mechanism is unchanged. Upon that it is understandable that the enhanced electronic conductivity due to the substitution of a small amount of high valence metal ions for lithium ions does not lead to improved battery performance. As the heavy high valence metal ions in the Li sites will block the one-dimensional diffusion pathways, the ionic conductivity is decreased, which is certainly harmful to the battery performance. It is also reasonable that $\delta=0.5$ configuration is the most favorable configuration for the case of $\text{Na}_{0.5}\text{CoPO}_4$. Since the motion of Na ions is only free to move in one dimension, with the Coulomb interaction among the Na ions, they will distribute as far away as possible, which finally leads to the $\delta=0.5$ configuration.

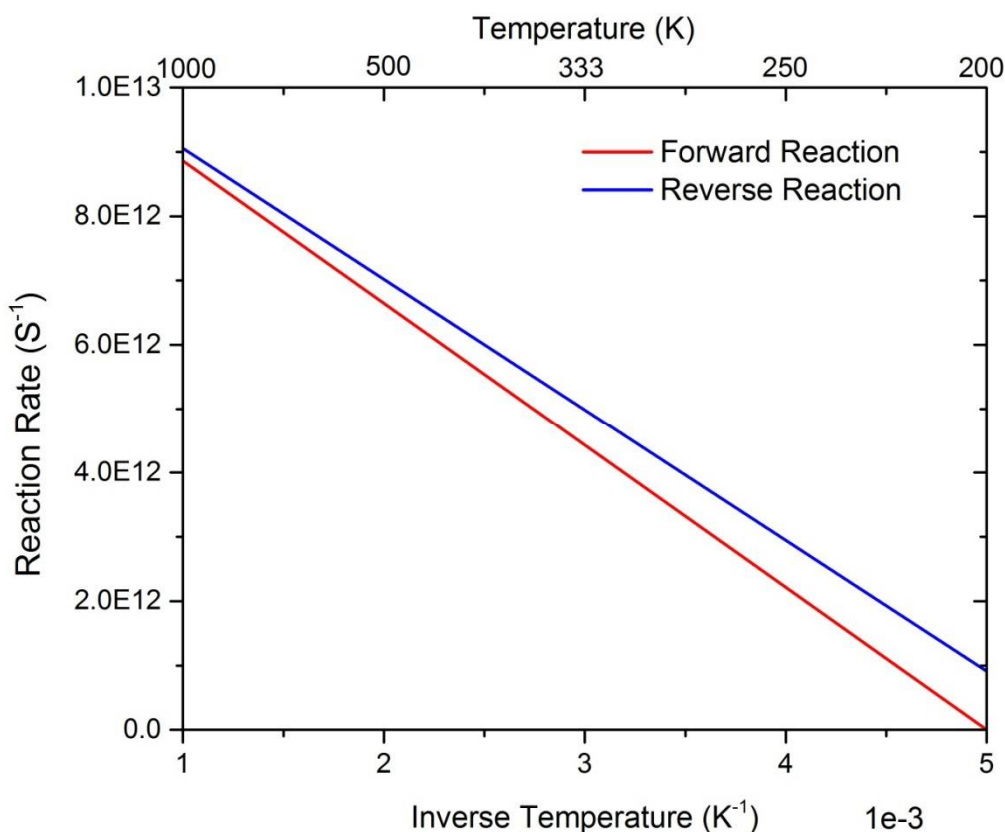


Fig. 4 Calculation of Reaction Rates using Harmonic Transition State Theory.

Calculating Reaction Rates using Harmonic Transition State Theory (HTST) employed here HTST is derived from a more general formalism known as transition state theory (TST). TST works by defining a transition state (a hyperplane) that separates the reactant from the products. Then the reaction rate is calculated as the probability of finding the system in the transition state relative to the entire reactant state, multiplied by the rate of crossing from the reactant region to the product region at the transition state

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Table 2 energy barriers (eV) and reaction rates (s^{-1}) calculated at 300 K for Na diffusion in Na_xCoPO_4 ($\delta=0.5$ and 1) along the B and C directions.

Direction	Barrier	k_{HTST}
B	0.42	3.1×10^6
C	2.25	1.8×10^{-26}

In general, TST is difficult to use, because it requires a definition of the transition state hyperplane. Additionally, calculating the probability of being at the transition state requires evaluating the full partition function of the transition state region and the reactant region, which is computationally prohibitive when using density functional theory, and challenging even for fast classical potentials. Fig. 4 shows Arrhenius plot of the temperature dependence of the HTST rate. An Arrhenius plot is the $\log(\text{rate})$ vs $1/T$. When the temperature dependence is plotted this way, the plots will always be straight lines. The slope of the line is $-\Delta E/k_B$ and the y-intercept is the prefactor. From the plot, it is easy to interpret that the prefactor is the maximum possible rate predicted by HTST. Here, we can calculate the forward and reverse reaction rates for your diffusion mechanism. In this case we will find these two values to be very close to each other because the initial and final states are essentially equivalent.

IV. CONCLUSION

In summary, our first principle calculations show that Na diffusion in olivine $NaCoPO_4$ is one dimensional, which explains why the enhanced electronic conductivity through Na site doping did not improve the electrochemical performance for $NaCoPO_4$ as the cathode material. The diffusion energy barrier in $CoPO_4$, a little lower than in $Na_{0.5}CoPO_4$, is about two times higher than in $NaCoPO_4$, which agrees well with the experiments. The directly observed diffusion trajectory from full *ab initio* MD simulations confirmed the one-dimensional diffusion pass way.

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