Magnetic, electrochemical and thermoelectric properties of P2 - Na$_x$(Co$_{7/8}$Sb$_{1/8}$)O$_2$

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We theoretically investigated the electronic, electrochemical and magnetic properties of Sb doped Na$_x$CoO$_2$ ($x = 1, 0.75$ and $0.50$). Sb$_{Co}$ dopants adopt +5 oxidation state in Na$_x$CoO$_2$ host lattice for all Na concentrations ($x$). Due to high oxidation states, Sb$^{5+}$ strongly repels Na ions and therefore it decreases the electrochemical potential (vs. Na/Na$^+$). The electrons introduced by Sb$^{5+}$ localize on nearby Co ions creating Co$^{2+}$ species which are absent in undoped Na$_x$CoO$_2$. Co$^{2+}$ ions reduce the spin entropy flow decreasing the Seebeck coefficient in the Sb doped compounds. The results can be generalized to other dopants with high oxidation state.

Keywords: Density functional theory, Sodium cobaltate, Magnetism, Thermoelectric, Sodium ion battery.

INTRODUCTION

Sodium cobaltate (Na$_x$CoO$_2$) is an interesting and promising compound for high efficiency thermoelectric [1] and sodium ion battery applications [2]. This compound also exhibits a rich magnetic and structural phase diagrams [3-4]. As demonstrated in FIG. 1, the primitive cell of P2-Na$_x$CoO$_2$ lattice is made of two alternating Na layers and edge-sharing CoO$_6$ octahedra. Due to its frustrated triangular nature, the CoO$_2$ layer in Na$_x$CoO$_2$ creates a large spin entropy flow [5] and which results in a large Seebeck coefficient [6]. From materials engineering viewpoint, controlling Na concentration ($x$) has been the primary technique to tailor the properties of Na$_x$CoO$_2$ for the desired applications. However, given the volatile nature of Na ions [7], establishing the precise property-structure relationship experimentally is somehow challenging. This experimental difficulty has motivated ongoing theoretical investigations into the structural and electronic properties of pristine Na$_x$CoO$_2$ [8-11].

Doping Na$_x$CoO$_2$ with other elements is another plausible method to improve the sodium cobaltate’s thermoelectric [12-13] and electrochemical properties [14-15]. Nonetheless, further progress in realizing high performance functional applications of the doped Na$_x$CoO$_2$ compounds requires an accurate understanding of the electronic structure of the doped P2-Na$_x$CoO$_2$. However, due to complex crystal structure of and strong electronic correlation in Na deficient sodium cobaltate, the theoretical aspects of doped Na$_x$CoO$_2$ have not been fully explored. Accordingly, in this work, we study how Co’s substitution with Sb influences the electronic behavior of Na$_x$CoO$_2$. Sb doping was particularly chosen as it has recently shown to improve the electrochemical performance of other layered cathode materials [16,17]. Some of the conclusions drawn here can be applied to predict the magnetic, electrochemical and thermoelectric properties of Na$_x$CO$_2$ compounds in which dopants with high oxidation state partially replace Co.

COMPUTATIONAL AND SYSTEM SETTINGS

Spin-polarized density functional calculations based on the projector augmented wave method [18,19] were performed with VASP [20,21]. Generalized gradient approximation (GGA) based on Perdew-Wang formalism [22,23] was applied to approximate the exchange-correlation functional. The energy cutoff was set to be 500 eV . Brillouin zone sampling for the supercells was carried out by choosing a k-point grid with 0.05 Å$^{-1}$ spacing between the k points generated by Monkhorst-Pack scheme [24]. Orbital projected density of states (DOS) were calculated using LOBSTER package [25,26]. To improve accuracy, we added on-site Coulomb ($U$) and exchange ($J$) interaction terms of $U = 6$ and $J = 1$ eV ($U_{eff} = 5$ eV) to Co 3d electrons using Dudarev’s approach [27]. Among many values reported for $U$ and
TABLE I. The calculated structural and electrochemical properties of Na$_x$CoO$_2$ and their comparison to earlier works. The calculated lattice parameters deviate from the experimental values by less than 1% and the potential (vs. Na/Na$^+$) calculated with $U_{\text{eff}} = 5$ eV deviates from the measurement by less than 3%.

| Compound | Na$_x$CoO$_2$ | Na$_{0.75}$CoO$_2$ | Na$_{0.5}$CoO$_2$ |
|----------|----------------|-------------------|-------------------|
| $a$ (Å)(This work) | 2.906 | 2.890 | 2.834 |
| $c$ (Å)(This work) | 10.566 | 10.899 | 11.171 |
| $a$ (Å)(Experiment) | 2.882 | 2.832 | 2.8150 |
| $c$ (Å)(Experiment) | 10.492 | 10.99 | 11.129 |

Potential vs. Na/Na$^+$, ($U_{\text{eff}} = 5$ eV)

| Potential | Na$_x$/Na$^+$, ($U_{\text{eff}} = 5$ eV) |
|-----------|---------------------------------|
| — | 2.396V |
| — | 2.880V |

Potential vs. Na$_x$/Na$^+$, ($U_{\text{eff}} = 4$ eV)

| Potential | Na$_x$/Na$^+$, ($U_{\text{eff}} = 4$ eV) |
|-----------|---------------------------------|
| — | 1.295V |
| — | 2.501V |

Experimental average potential

| Na$_1$/Na$_2$ | (This work) 0 0.5 1 |
|----------|----------------|---|
| Na$_1$/Na$_2$ (Others) | — | — |

$U_{\text{eff}}$ = 4 eV)

Co from the bottom CoO$_2$ layer with the Sb dopant. We then relaxed the internal coordinates of all ions in the supercell while fixing the lattice constants to the calculated values of undoped Na$_x$CoO$_2$.

RESULTS AND DISCUSSION

It has been established that Sb ions are always stabilized by substituting a Co ion for a wide range of x in the Na$_x$CoO$_2$ host lattice. Now, we examine how Sb behave electronically in Na$_x$CoO$_2$ host lattice. Sb ions generally adopt two stable oxidation states; Sb$^{5+}$ and Sb$^{3+}$. Sb$^{5+}$ ion is isovalent to Co$^{3+}$ therefore Co$^{3+}$ substitution with Sb$^{3+}$ does not alter the carrier density in the host system. This means that in Na$_1$CoO$_2$:Sb$^{3+}$, all Co ions are in +3 oxidation state (t$_{2g}^6$e$_{g}^0$). In Na$_{0.75}$CoO$_2$:Sb$^{3+}$, two Co$^{3+}$ convert to Co$^{4+}$ (t$_{2g}^5$e$_{g}^0$) to bear the holes generated by Na extraction. Similarly, in Na$_{0.5}$CoO$_2$:Sb$^{3+}$, four Co ions are in +4 oxidation state. Sb$^{5+}$, on the other hand, introduces two electrons that would be borne on Co ions in an opposite manner to any holes created by Na extraction. Consequently, in Na$_{0.75}$CoO$_2$:Sb$^{5+}$, two Co$^{3+}$ (t$_{2g}^5$e$_{g}^0$) ions convert to Co$^{2+}$ (t$_{2g}^6$e$_{g}^1$). In Na$_{0.75}$CoO$_2$:Sb$^{5+}$, however, there are two possibilities. First, the two extra elec-

FIG. 1. The top and side views of Na$_x$CoO$_2$ P63/mmc crystal structure. Co ions occupy 2a sites (0,0,0), O ions occupy 4f sites (1/3, 2/3, z). In Na$_x$CoO$_2$, all Na ions occupy Na2 sites which are equivalent to 2d Wyckoff position (2/3, 1/3, z). For smaller Na content, some Na ions occupy Na1 sites with 2b Wyckoff representation (0, 0, z). 2b site are marked by brown circles for clarity.

J in the literature, the chosen $U_{\text{eff}}$ value reproduces the charge disproportionation of the Co ions and as shown in Table I predicts more accurate electrochemical potential (vs. Na/Na$^+$) for Na$_x$CoO$_2$. We could nonetheless reproduce the charge disproportionation with smaller $U_{\text{eff}}$ of 4 eV but this value greatly underestimates the electrochemical potential. Furthermore, for Na$_{0.5}$CoO$_2$:Sb, we compared the accuracy of $U_{\text{eff}} = 5$ eV against HSE03 functional. Both methods resulted in similar orbital alignment for Co and Sb ions and similar charge densities indicating the adequacy of the chosen $U_{\text{eff}}$.

The unit cells of the desodiated Na$_x$CoO$_2$ ($x = 0.75$ and 0.5) were constructed by removing Na ions from the pristine Na$_x$CoO$_2$ (shown in FIG. 1). In desodiated Na$_x$CoO$_2$, a Na ion can occupy either Na1 site or a Na2 site. The Na1 site is located above the Co ions in CoO$_2$ layer and the Na2 site is located in above the center of the triangle formed by three Co ions. Na1 and Na2 correspond to 2b and 2d Wyckoff positions respectively in a hexagonal P63/mmc lattice as shown in FIG. 1. The arrangement of Na in Na1 and Na2 sites depends on Na concentration. In this work, we adopt the Na arrangement obtained in our previous work. Table I contains the calculated lattice parameters and the dimensions of the of Na$_x$CoO$_2$ unitcell with respect to the Na$_x$CoO$_2$ primitive cell. We used a 4$a$ × $2a$ × 1$c$ Na$_x$CoO$_2$ and a $2a$ × $1a$ × 1$c$ Na$_{0.5}$CoO$_2$ supercells and the unitcell of Na$_{0.75}$CoO$_2$ to simulate doped compounds. All doped supercells contained seven Co, one Sb and 16 O ions as described in FIG. 2. For the sake of clarity, we always substituted a
trons generated by Sb\(^{5+}\) substitution compensate for the two holes created by Na removal leaving all Co ions in Na\(_{0.75}\)CoO\(_2\):Sb\(^{5+}\) at +3 oxidation state \((t_{2g}^6 \delta_g^0)\). The other possibility is that the hole created by Na extraction from the top Na layer localizes on the neighboring Co from the top CoO\(_2\) layer converting a Co\(^{3+}\) to Co\(^{4+}\) while simultaneously, the hole created by Na extraction from the bottom CoO\(_2\) layer converts a Co\(^{2+}\) to back a Co\(^{3+}\). In this scenario, there is one Co\(^{4+}\) \((t_{2g}^2 \delta_g^0)\) in the top CoO\(_2\) layer and one Co\(^{2+}\) \((t_{2g}^6 \delta_g^0)\) in the bottom CoO\(_2\) layer. In Na\(_{0.5}\)CoO\(_2\) Sb\(^{5+}\), the two electrons from Sb\(^{5+}\) convert two nearby Co\(^{4+}\) ions from the same CoO\(_2\) layer that contains the Sb dopant back to Co\(^{3+}\).

Table II shows all different possible oxidation states of Co ions and the relative total energy of Sb\(^{3+}\) and Sb\(^{5+}\) doped Na\(_x\)CoO\(_2\). For all x values, our results indicate that the Sb\(^{5+}\) is more stable than Sb\(^{3+}\) when substituting a Co in the Na\(_x\)CoO\(_2\) host lattice. One possible explanation for this trend is that the ionic radius of Sb\(^{5+}\) in octahedral coordination is 0.60 Å which is closer to the ionic radius of Co\(^{3+}\) in Na\(_x\)CoO\(_2\) which is 0.55 Å\). The ionic radius of Sb\(^{3+}\) in octahedral coordination is 0.76 Å which is considerably larger than Co\(^{3+}\)'s radius therefore its substations would lead to large internal lattice stress. Furthermore, for \(x = 1.00\) and 0.75, the substitution of Co with Sb adds electrons to antibonding Co \(e_g\) states which are \(\sim 2.3\) eV higher than the \(t_{2g}\) states. In this case, Sb\(_{Co}\) dopant is, nonetheless, still more stable than Na substituting configurations as the formation energy of the latter is generally 2.2 to 2.8 eV higher than Co substituting configurations\[35\].

FIG. 3 shows the total and partial density of states of Na\(_x\)CoO\(_2\):Sb\(^{5+}\). A common feature among all three Sb doped compounds is the large crystal field splitting among Co\(^{3+}\) \(t_{2g}\) and \(e_g\) states as marked with grey arrows. This prediction agrees with the well-known Co's octahedral splitting of \(\sim 2.3\) eV\[37\]. Furthermore, the Fermi level of both Na\(_3\)CoO\(_2\):Sb\(^{5+}\) and Na\(_{0.5}\)CoO\(_2\):Sb\(^{5+}\) is located in zero DOS region indicating that the Sb doping in these two compounds does not introduce metallic conduction. However, the Fermi level in Na\(_{0.75}\)CoO\(_2\) crosses an \(e_g\) sub-band (marked with a brown arrow in Fig. 3(b)) that is located near the main valence band creating a metallic conduction in a similar manner to the undoped Na\(_{0.75}\)CoO\(_2\)[38]. Additionally, the filled 5p states gravitate towards the bottom of the valence states indicating Sb’s high oxidation state of +5. In Na\(_3\)CoO\(_2\):Sb\(^{5+}\) and Na\(_{0.75}\)CoO\(_2\):Sb\(^{5+}\)\[FIG. 3(a) and (b)], Co\(^{5+}\) \(e_g\) states experience further crystal field and ferromagnetic exchange splittings. As a result, filled \(e_g\) states are positioned just above the fully filled Co\(^{3+}\) \(t_{2g}\) states constituting antibonding states while the rest of the \(e_g\) states are located above the Fermi level. In Na\(_{0.75}\)CoO\(_2\):Sb\(^{5+}\) and Na\(_{0.5}\)CoO\(_2\):Sb\(^{5+}\)\[FIG. 3(b) and (c)], on the other hand, all \(t_{2g}\) states split and locate above the Fermi level.

The spin density of the ground states of Sb doped Na\(_x\)CoO\(_2\) compounds is presented in FIG. 2. In all compounds, we see that the electrons of the of the Sb\(^{5+}\) ion localize on the neighboring Co ions. In Na\(_x\)CoO\(_2\):Sb\(^{5+}\), there are two Co\(^{2+}\) ions neighboring Sb\(^{5+}\). In Na\(_{0.75}\)CoO\(_2\), a hole created by Na vacancy in the bottom layer neutralizes the electron on one of the Co\(^{2+}\) ion, nonetheless, the second Co\(^{2+}\) retains its electron while second Na vacancy from the top layer oxidizes a nearby Co\(^{3+}\) to Co\(^{4+}\). In Na\(_{0.5}\)CoO\(_2\):Sb\(^{5+}\), the two Na vacancies from the bottom layers neutralize the electrons on the two Co\(^{2+}\) ions neighboring to Sb\(^{5+}\) while the Na vacancies in the top layer are oxidized by the Na vacancies in the top layer. Furthermore, we see that the magnetic moment bearing Co ions couple ferromagnetically with each other when they are located in the same CoO\(_2\) layer and antiferromagnetically when they are located in different CoO\(_2\) layers. This trend is similar to that of undoped Na\(_x\)CoO\(_2\) which exhibits in-plane ferromagnetism and out of plane antiferromagnetism (A-type) for a considerable range of \(x\)[39-41].

To examine the strength of magnetic coupling, we recalculated the total energy of the Sb\(^{5+}\) doped compounds under constraints that fixed the spin coupling to the opposite settings of the ground states presented in FIG. 2. We found that the total energy of Na\(_1\)CoO\(_2\):Sb\(^{5+}\) increased by 61.577 meV/f.u. (f.u. is formula unit) when the Co\(^{2+}\) ions were ferromagnetically coupled; the total energy of Na\(_{0.75}\)CoO\(_2\):Sb\(^{5+}\) increased by 68.551 meV/f.u. when the Co\(^{2+}\) and Co\(^{4+}\) had parallel spin alignment and the total energy of Na\(_{0.5}\)CoO\(_2\):Sb\(^{5+}\) increased by 65.336 meV/f.u. when the Co\(^{3+}\) ions in the top layer had antiferromagnetic alignment. Our results demonstrate that similar to the undoped Na\(_x\)CoO\(_2\), the in-plane and out-of-plane magnetic couplings are of the same magnitude[42].

To investigate the electrochemical activity of the Sb doped Na\(_x\)CoO\(_2\), we calculated the average voltage of the Na\(_x\)CoO\(_2\):Sb cathode as a function of Na content \(x\) using the following equation:

\[
V = -\frac{E^\prime (Na_xCoO_2:Sb) - E^\prime (Na_{x-y}CoO_2:Sb) - E^\prime (Na)}{(x-y) e}
\]

in which \(E^\prime (Na_xCoO_2)\) is the total energy of the Na\(_x\)CoO\(_2\) compound, \(E^\prime (Na)\) is the total energy of the elemental solid Na per atom and \(e\) is the electronic charge. We found that the average potential was 2.140 V for \(1 < x < 0.75\) and 2.373 V for 0.75 < \(x < 0.5\). These voltages are slightly smaller than that of the pristine compound for which we calculated voltages of 2.396 V for 1 < \(x < 0.75\) and 2.880 V for 0.75 < \(x < 0.5\). The slight decrease in the potential may have been caused by Sb\(^{5+}\) stronger electrostatic repulsion towards Na ions which facilitates easier Na extraction.

Now let's examine how dopants affect the thermoelectric performance of the sodium cobaltate. The Seebeck
FIG. 2. Spin densities ($\rho$) at Co sites in Sb doped Na$_x$CoO$_2$ structures. Na, O, Co and Sb ions are represented by yellow, red, blue and brown spheres respectively. The green circles denote the sites from which Na ions were vacated. Yellow and cyan iso-surfaces correspond to the up spin and down spins respectively. The iso-surfaces were adown at $\rho = 0.025e/\text{Å}^3$.

FIG. 3. Total and partial density of states of the Sb doped Na$_x$CoO$_2$ compounds. In the top panels, black, red and purple lines correspond to the total, O 2p, and Na 3s states. In the middle panels, gray and green lines correspond to Co$^{3+}$ 3d and Sb states. In the bottom panels, the blue and magenta lines correspond to the Co$^{2+}$ 3d and Co$^{4+}$ states. Sb, Na, Co$^{2+}$ and Co$^{4+}$ states were magnified for clarity.

effect in Na$_x$CoO$_2$ is driven by the spin entropy flow between Co$^{3+}$/Co$^{4+}$ according to the modified Heike’s formula for $S$ [43]:

$$S = -k_B \frac{e}{e} \ln \left[ \frac{g(\text{Co}^{3+})}{g(\text{Co}^{4+})} \frac{t}{1-t} \right].$$

Here $k_B$ is the Boltzmann constant, $e$ is the electron charge, $t$ is the concentration of Co$^{3+}$ ions and $g$ is electronic degeneracy of the Co ions. The electronic degeneracy ($g$) of an ion equals to the different possible ways in which electrons can be arranged. Consequently, $g$ is the product of spin degeneracy ($g_{\text{spin}}$) and orbital ($g_{\text{orbital}}$) degeneracy: $g = g_{\text{spin}} \cdot g_{\text{orbital}}$. $g_{\text{spin}}$ equals to $2\zeta + 1$ where $\zeta$ is the total spin number and $g_{\text{orbital}}$ is the number of valid permutations for distributing the electrons.
spin entropy flow between Co one expects that Sb doping in Na4+ concentration of Co NaS compound but Sb of S value in pristine NaCoO2-Sb2+ layers with Co2+ ions. Since the g and t values in Eq. 2 yields S = 40.50 µV/K. We should remember that in pristine Na0.5CoO2, all Co ions are in +3 oxidation state, there is no spin entropy flow and therefore S = 0. In Na0.75CoO2-Sb2+, the Seebeck effect is driven by the spin entropy flow between Co3+/Co4+ and Co3+/Co2+ ion pairs. Since the g(Co2+) is smaller than g(Co3+), one expects that Sb doping in Na0.75CoO2-Sb2+ would decrease S with respect to S in pristine compound. In Na0.5CoO2-Sb2+, Co2+ ions are no longer present in the compound but Sb5+ dopant instead greatly decreases the concentration of Co4+. Consequently, we obtain an S value of 75.44 µV/K which is less than half of the value of S value in pristine Na0.5CoO2 which is 154.40 µV/K.

### CONCLUSIONS

We demonstrated that Sb dopant in Na5.75CoO2 adopt the highest possible oxidation state, in this regard, is acts similar to Eu3+, Ni4+ [44], Cu2+ [45] and Ru4+ [46] dopants. The electrons generated by Sb5+ high oxidation state, localize on the neighboring Co ion instead of being delocalized over the valence band. This phenomenon results in the creation of Co2+ ions which do not occur in Na5.75CoO2. Magnetically, Co2+ ions behave similarly to Co4+ as they couple ferromagnetically within the same CoO2 layer and couple antiferromagnetically across CoO2 layers with Co4+ ions. The higher electrostatic repulsion between Sb5+ and the Na+ ions facilitates easier Na+ extraction that eventually results in a slight decrease in the electrochemical potential. We therefore anticipate W6+, Bi5+, Sn4+ [45] dopants having similar effect in reducing the Na extraction potential.

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**TABLE II. Number of electron bearing Co ions (Co2+) and number of hole bearing Co (Co4+) and the relative energy in Na5.75CoO2-Sb2+ and Na5.75CoO2-Sb5+. The relative energy is presented with respect to the most stable compound for a given Na content.**

| System       | No. Co2+ | No. Co4+ | Total Energy (eV/f.u.) |
|--------------|----------|----------|------------------------|
| Na5.75CoO2-Sb2+ | 2        | 5        | 5 2 0 0.855            |
| Na5.75CoO2-Sb5+ | 0        | 7        | 0 0 0.587              |
| Na5.75CoO2-Sb2+(1) | 1       | 5        | 1 2 0 0.319            |
| Na5.75CoO2-Sb2+(2) | 0       | 7        | 0 0 0.319              |
| Na5.75CoO2-Sb5+ | 0        | 5        | 2 2 0 0.115            |
| Na5.75CoO2-Sb5+ | 0        | 5        | 5 2 2 0.115            |
| Na5.75CoO2-Sb5+ | 0        | 3        | 4 4 0.115              |

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