First-principle calculation for inherent stabilities of \( \text{Li}_x\text{CoPO}_4, \text{Na}_x\text{CoPO}_4 \) and the mixture \( \text{Li}_x\text{Na}_y\text{CoPO}_4 \)

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**ABSTRACT**

We have synthesized NaCoPO\(_4\) and LiCoPO\(_4\) via microwave-assisted solvothermal synthesis. The local atomic structure around Co atoms was characterized by means of Co K-edge XANES spectroscopy. Using X-ray diffraction, we have identified two NaCoPO\(_4\) phases with Pnma and P6\(_3\) space groups (lattice parameters \( a = 10.26 \) Å, \( b = 5.93 \) Å, \( c = 4.74 \) Å, and \( a = 10.16 \) Å, \( b = 10.16 \) Å, \( c = 23.87 \) Å, respectively) and one LiCoPO\(_4\) phase with Pnma space group with lattice parameters \( a = 10.22 \) Å, \( b = 5.93 \) Å and \( c = 4.71 \) Å. Within GGA + U approximation we have calculated the variation of the cell volume versus Li foil and atomic Bader charges for a wide range of alkali metal concentration in the material. Considering the low cost of the material and high intercalation voltage the synthesized sodium-based material is a good candidate for novel cathode materials.

1. Introduction

The problem of energy storage and recyclable use of small and powerful accumulators is the main challenge for the intense development of electric vehicles, mobile devices, autonomous robots\([1]\). Lithium-ion batteries (LIB) have proved their reliability in many applications, such as uninterruptible power supply systems, photovoltaic power generation, energy recovery systems for industrial machinery, and transportation systems\([1–3]\). Nevertheless, huge research efforts are still concentrated on developing novel classes of electrode materials, mainly high voltage cathode ones. LiFePO\(_4\) with olivine structure, which was first conveyed by Padhi et al.\([4]\), has received excessive interest as LIB cathode material. It is one of the most promising materials amongst other olivines and is extensively studied due to low cost, high reversibility, thermal stability and safety\([5]\). However, LiFePO\(_4\) has some deficiencies, such as low potential (3.4 V) and small packing density (owing to the inclusion of large-volume carbon), which lead to low specific energy density (580 W h kg\(^{-1}\)).

To overcome these difficulties other transition metals were introduced in the olivine structure of LiMPO\(_4\), M = Mn, Fe, Co, or Ni. Among them, LiCoPO\(_4\) has a large theoretical capacity (167 mA h g\(^{-1}\)) and high specific energy density (800 W h Kg\(^{-1}\))\([6]\). This material has a high potential of 5.75 V as follows from theoretical GGA + U calculations\([7]\) compared to 4.8 V vs. Li/Li\(^+\) measured experimentally\([8]\). LiCoPO\(_4\) was already applied in 18650 batteries, and Howard et al. appraised the LiCoPO\(_4\) cost to be 142$ kW\(^{-1}\) h\(^{-1}\), in comparison to 198 and 158$ k/Wh for LiCoO\(_2\) and LiFePO\(_4\) respectively\([9,10]\). Even though attractive for high energy and high power applications, large scale use of LiCoPO\(_4\) as a cathode has been hindered by the unsatisfactory cycle stability and rate performance\([10]\). The latter fact was addressed theoretically and Osins et al. showed that stability of LiCoPO\(_4\) can be improved by Fe doping. In a mixed compound LiFe\(_{1-x}\)Co\(_x\)PO\(_4\) the stability upon delithiation increases when Fe concentration increases\([11]\).

The high cost of all Li-based batteries is related to the expensive sources of Li. Worldwide industrial applications of Li-based power sources lead to the shortage of Li raw materials and hence even higher production costs\([12]\). Higher abundance of Na in nature and its low cost...
lead to an advantage when a large amount of alkali is demanded for large-scale applications. Na-ion batteries can offer more energy density than Li-ion ones and can work at elevated temperatures [13]. For sodium-ion insertion, negative electrodes based on hard carbons have brilliant properties with up to 350 mA h g⁻¹ capacity [14,15].

For the synthesis of LiMPO₄ materials (M = Fe, Co, Ni, Mn) many techniques were applied, such as sol-gel method [16,17], hydrothermal synthesis μ [18], MW heating [19–21], and other [20,22–24]. For example, for LiFePO₄, one of common synthesis methods includes either solid-state approach and/or solution-based approach [23]. In the present work, we have used MW synthesis technique to reduce the time of heating and particle size. This strategy is robust not only for decreasing the time of reaction, but can also be adjusted in order to produce standized nanoparticles on the industrial scale [25]. In conventional synthesis 3d metal phosphates with Na form an electrochemically inactive matricite structure which has no cationic sodium diffusion. In a solid state or mecanochemical reaction three phases – α, β and γ-NaCoPO₄ can be obtained [26]. Recently Gutierrez et al. [27]synthesized electrochemically active Red-phase of NaCoPO₄ by microwave-assisted method. The material showed stable capacity in the range 35–40 mA h g⁻¹ for the 40 cycles with a voltage range 4–4.5 V vs. Na/Na⁺. The Red-phase categorizes as one of the very few high voltage cathodes presently available for sodium-ion batteries. Following the success of LiMPO₄ materials the similar Na-based compound with olivine structure, NaMPO₄ is a potential better candidate for sodium ion batteries.

In present work we have synthesized NaCoPO₄ both in β- and Pnma phases using protocol from LiCoPO₄ synthesis. From the theoretical point of view, we introduce a routine for practical construction of novel mixed LiₓNa₁₋ₓCoPO₄ material by sequential substitution of Li to Na. We discuss its electrochemical properties and formation energies. GGA + U simulations for a large supercell of the LiₓNa₁₋ₓCoPO₄ structure allowed accurate estimations of the volume changes and working potentials of the material. We show that introducing sodium in the structure of the material increases the operational voltage from vs. Na/Na⁺ [28]. For the first time we calculated accurate Bader charges on all atoms in the unit cell and show their variation across the insertion and extraction cycles of lithium and sodium. We report the inherent relative stabilities of Li₁ₓNaₓCoPO₄ and Li-CoPO₄ (x = 0, 0.25, 0.5, 0.75, 1) and Na-CoPO₄ (x = 0.25, 0.5, 0.75, 1) and show that sodium might play a significant role in the electrochemical performance of the cathode material.

2. Methods

Spin-polarized density functional calculations were performed with the VASP 5.2 program package via projector augmented wave (PAW) method. For every composition x,y in LiₓNa₁₋ₓCoPO₄ cell volume and atomic positions were optimized in a two-step procedure. 2 × 2 × 1 supercell with 112 atoms, constructed from the orthorhombic structure for LiCoPO₄ with Pnma space group [28] was used as an initial approximation. Then at a first step, lattice parameters were relaxed while unit cell angle and atomic positions were constrained to their initial values. In a second step, atomic positions were relaxed for fixed, optimized lattice parameters. A kinetic energy cutoff 520 eV was used for the plane-wave basis set. 3 × 3 × 3 K-point meshes were automatically generated according to the Monkhorts-Pack scheme. The PBEsol functional [29] was used to treat exchange-correlation effects while on-site Coulomb interactions were corrected by the GGA + U approach via Dudarev scheme [30]. We used U = 5.05 eV for Co [7]. For optimized structures, we calculated atomic charges using Bader method. The Bader charge is calculated for the all-electron density recovered from the POTCAR file using the LAECHG = TRUE [31]. keyword to obtain core electron densities from the calculation [32].

For synthesis the following starting materials were purchased from Alfa Aesar and used without purification: lithium phosphate monobasic LiH₂PO₄, sodium phosphate monobasic dihydrate NaH₂PO₄·2H₂O, lithium acetate monohydrate LiC₂H₃O₂·H₂O (LiAc), sodium acetate monohydrate NaC₂H₃O₂ (NaAc), cobalt(II) oxalate dihydrate CoC₂O₄·2H₂O (CoOx), glucose C₆H₁₂O₆, ethylene glycol (EG). Ultra-pure water (18 MΩ cm) was produced by SimplicityUV (Millipore) from distilled water. In a typical synthesis Li(Na)H₂PO₄, Li(Na)Ac, CoOx and glucose were dissolved in water. Then EG was added, and the reaction mixture was placed into Teflon vessel, closed hermetically and heated in MW oven CEM Mars 6 at 220 °C for 3 h with magnetic stirring. Molar ratio of mixture components was Li(Na)H₂PO₄:Li(Na)Ac:CoOx:glucose:water:EG = 1.17:1.83:1.05:72.4:8.119:4. After cooling down precipitate was separated by centrifugation at 20000 rpm, washed with water three times and dried at 60 °C overnight. The as-synthesized powders were annealed in air at 700 °C for 8 h.

Powder XRD patterns were collected with a laboratory Bruker D2 Phaser diffractometer using Cu Kα1 radiation in the 2θ range 20–80°. The XRD patterns were analyzed by means of RIETVELD refinement in FullProf software [33]. Co K-edge X-ray absorption near edge spectra (XANES) of LiCoPO₄ and NaCoPO₄ samples were measured with Rigaku R-XAS Looper laboratory spectrometer. All measurements were performed in transmission geometry with Ge (311) crystal as a monochromator, providing energy resolution ΔE = 1.9 eV. The incident beam intensity was measured by Ar-filled (300 mbar) ionization chamber, transmitted intensity – by scintillation counter with a photomultiplier tube. The samples for measurements were diluted with 50 mg of dry cellulose powder and pressed into pellets. The amount of sample for a pellet was calculated using XAFSmass software [34]. Spectra for reference compounds (CoO, Co₃O₄) were measured the same way to determine the charge state of Co using the chemical shift rule.

3. Results and discussion

Fig. 1 shows the XRD patterns of the synthesized materials. After reactions we obtained Pnma phase for LiCoPO₄ with lattice parameters 10.22, 5.93 and 4.71 Å which are consistent with previously reported results [35]. NaCoPO₄ has two phases as shown in Fig. 1b. The first phase has Pnma symmetry and the second has P6₅ symmetry and different lattice parameters. Experimental lattice parameters for the as synthesized sample were further confirmed by means of theoretical DFT calculations. Table 1 shows a comparison between the calculated lattice parameters and experimental ones. The difference between experimental and theoretical lattice parameters for LiCoPO₄ is about 0.2% which is in the order of magnitude of the accuracy of DFT GGA-PBE approximation. For NaCoPO₄ we observe larger differences between experimental data and calculations due to different stoichiometry observed in the synthesized samples – i.e. real composition of synthesized material was NaₓCoPO₄ with x < 1. We further confirm this fact by using Co K-edge XANES spectroscopy.

Due to higher ionic radius insertion of Na in the cathode material increases the cell parameters of the system. The cell volume per formula unit for NaCoPO₄ reaches 303.396 Å³ and is larger than one of LiCoPO₄ by 6.2%. These results agree with the difference between ionic radii of Li and Na which is 74.5%. Unit cell volumes for the LiNaCoPO₄ system with different concentrations of alkali metals are shown in Fig. 2. The calculation reproduces the experimental structural parameters of pure LiCoPO₄ with the accuracy of 0.2%. As shown in Table 1, the volume of LiₓCoPO₄ increases along with the ratio of Li by 0.37% between x = 0.25 and 0.5, and by 0.26% between x = 0.5 and 0.75, but for x from 0.75 to 1 the change is very insignificant. These results agree with in situ XRD measurements obtained by Ref. [35].

The chemical bond energies were calculated using Equation (1), where E(Li), E(Co), are the total energies calculated for a single atom in the supercell. For instance, the chemical bond energy for 2x2 LiCoPO₄ supercell can be calculated according to the following equation:

$$
\Delta E = E(\text{Li}_2\text{CoPO}_4) - x\cdot E(Li) - 16\cdot E(Co) - 16\cdot E(P) - 64\cdot E(O)
$$
where $x$ is the number of Li atoms in the supercell. This value is further divided by 16 to obtain bond energy per formula unit. To obtain the intercalation energies for different stoichiometries and hence the working cell potential we utilized following reactions:

$$\text{CoPO}_4 + x\text{Li} \rightarrow \text{Li}_x\text{CoPO}_4$$

$$\text{CoPO}_4 + \text{Na}_{1-x} + x\text{Li} \rightarrow \text{Li}_x\text{Na}_{1-x}\text{CoPO}_4$$

$$\text{CoPO}_4 + x\text{Na} \rightarrow \text{Na}_x\text{CoPO}_4$$

Where energies for Na and Li were calculated for metallic species. From Fig. 3a the chemical bond energy per formula unit for Li$_x$CoPO$_4$ equals $-35.31$ eV when $x = 1$. When 25% of lithium has been removed the value increased by 1.56 eV per formula unit indicating decreasing of the stability. Similarly, when 25% of Na were removed from NaCoPO$_4$ the resulting value of chemical bond energy increased by 1.53 eV per formula unit. That means the LiCoPO$_4$ and NaCoPO$_4$ show similar behavior.

During charge lithium ions are extracted from the LiCoPO$_4$ cathode material and deposited on the metallic Li anode. During the discharge, Li-ions are removed from the anode to cathode. Aydinol et al. [37] presented a theoretical method for calculation of the average voltage of

\[ \text{Li}_x\text{Na}_{1-x}\text{CoPO}_4 \]

\[ x (\text{Li}) \quad y (\text{Na}) \quad \text{Theory} \]

\begin{tabular}{cccc}
1.00 & 0.00 & 10.202 & 5.918 & 4.708 & 284.303 \\
0.75 & 0.00 & 10.201 & 5.918 & 4.708 & 284.281 \\
0.50 & 0.00 & 10.192 & 5.913 & 4.704 & 283.541 \\
0.25 & 0.00 & 10.179 & 5.905 & 4.698 & 282.465 \\
0.00 & 1.00 & 10.425 & 6.047 & 4.812 & 303.396 \\
0.00 & 0.75 & 10.361 & 6.011 & 4.782 & 297.886 \\
0.00 & 0.50 & 10.277 & 5.962 & 4.744 & 290.707 \\
0.00 & 0.25 & 10.215 & 5.926 & 4.715 & 285.420 \\
0.25 & 0.25 & 10.301 & 5.976 & 4.755 & 292.744 \\
0.50 & 0.50 & 10.323 & 5.99 & 4.765 & 294.589 \\
0.25 & 0.75 & 10.418 & 6.043 & 4.808 & 302.771 \\
0.25 & 0.50 & 10.301 & 5.976 & 4.754 & 292.709 \\
0.50 & 0.25 & 10.240 & 5.940 & 4.726 & 287.496 \\
0.25 & 0.25 & 10.220 & 5.928 & 4.717 & 285.837 \\

\textbf{Experiment} \\
Li$_2$Na$_{0.5}$CoPO$_4$ & 10.22 & 5.93 & 4.71 & 285.44 \\
Na$_2$CoPO$_4$ & 10.26 & 5.93 & 4.74 & 288.39 \\

10.16 & 10.16 & 23.87 & 2463.99
delithiation for the Li-ion cell. We applied this technique for LiCoPO$_4$, Na$_x$CoPO$_4$ and Li$_x$Na$_{1-x}$CoPO$_4$. The average lithiation/delithiation voltage (vs Li/Li$^+$) can be calculated using the Gibbs energy per Li added/removed during the reaction, as shown in Equation (3) [38].

$$V = \frac{-\Delta G}{F \Delta N_{Li}}$$

(3)

where $F$ is the Faraday constant, $\Delta N_{Li}$ is the amount of Li added/removed, and $\Delta G$ is the change in the Gibbs free energy due to intercalation which can be approximated by the intercalation energy from equation (2) [38]:

$$\Delta G \approx E_{int} = \frac{E(LiCoPO_4) - E(CoPO_4) - nE(Li)}{N_{Li}}$$

(4)

As follows from Fig. 3b the average voltage before delithiation for LiCoPO$_4$ equals 4.99 V vs. Li/Li$^+$ but after delithiation decreases to 4.61 V vs. Li/Li$^+$ close to experimental value 4.8 V vs Li/Li$^+$ [39]. On the other hand, the calculated voltage of NaCoPO$_4$ reaches 4.48 V Na/Na$^+$ as shown in Fig. 3b in agreement with the voltage value obtained by Gutierrez et al. [27]. However, upon a decrease in the amount of sodium down to 0.75 the voltage decreases to 4.30 V vs. Na metal, and increases to 4.45 V when $y = 0.5$ as shown in Fig. 3b. When we exchange 50% of Na by 50% of Li the calculated intercalation voltage of Li$_{0.5}$Na$_{0.5}$CoPO$_4$ equals to 4.9 V vs. Li/Li$^+$.

To analyze changes in atomic charges we have performed the Bader charge analysis for all atoms in the supercell upon discharge process. The analysis proves that the cobalt formal charge state can be assigned to Co$^{2+}$ for all atoms when $x = 1$ in Li$_x$CoPO$_4$ as shown in Fig. 4a. Upon Li removal, the corresponding number of Co atoms change their oxidation state to +3. This fact is indicated by a vertical error bar in

![Fig. 3. Energetics of the delithiation process of Li$_x$Na$_y$CoPO$_4$. (a) The chemical bond energy calculated according to equation (2) per formula unit for Li$_x$Na$_y$CoPO$_4$, where $(x = 0, 0.25, 0.5, 0.75$ and $1)$, $(y = 0, 0.25, 0.5, 0.75$ and $1)$. (b) Corresponding voltage profile during delithiation process in Li$_x$Na$_y$CoPO$_4$ calculated according to equation (3).]

![Fig. 4. (a) Calculated average Bader charge on Co atoms with respect to different ratio of Li in LiCoPO$_4$ supercell. Panels (b) and (c) show calculated average Bader charges on Li and oxygen atoms in the same cell. The error bars indicate variations of atomic charges within the supercell and they are largest for Co due to coexistence of Co$^{2+}$/Co$^{3+}$ ions.]

As shown in Fig. 7a experimental Co K-edge XANES spectrum for LiCoPO$_4$ matches the energy position of CoO therefore oxidation state of Co can be estimated as Co$^{2+}$. Fig. 7b compares experimental Co K-XANES spectra for LiCoPO$_4$ and NaCoPO$_4$. The overall similarity of these spectra suggests similar olivine structure for both phases. However, there are also important differences. NaCoPO$_4$ demonstrates the lower
intensity and broader main peak located at 7720 eV, which is indicative for the mixture of phases and distortions in the first coordination sphere of Co and for possible presence of two phases in agreement with XRD analysis (refined Pnma and P65 space groups). Fig. 7b contains theoretical simulations for pure LiCoPO4 and two phases of NaCoPO4: Na0.5CoPO4 in Pnma space group and NaCoPO4 with P65 space group. Sharp features of LiCoPO4 XANES show good agreement with theoretical simulation thus suggest that it contains only one phase in accordance to XRD data analysis. Simulations for Na0.5CoPO4 indicate that lower intensity of the main edge at 7715 eV and broad feature at 7760 eV arise from multiple superposition of spectra for Co2+ and Co3+ positions in the supercell (see Fig. S1 for spectra of inequivalent Co positions in the supercell). Tetrahedral coordination of Co in P65 phase (bottom blue curve) can be also responsible for the observed differences between NaCoPO4 and LiCoPO4.

Experimental spectra for LiCoPO4 and NaCoPO4 show similar positions of the absorption edge. Our model for NaCoPO4 includes phase with reduced stoichiometry of Na – i.e. Na0.5CoPO4. Higher average Co oxidation state in this phase should result in absorption edge shift which is not observed experimentally. We attribute this fact to the two effects which affect absorption edge position. First is the Co charge state. Second is the Co–O interatomic distances in the first coordination sphere. The latter decrease upon Co2+ - Co3+ transition. This effect can partially compensate the expected absorption edge shift. Experimental studies of...
NaCoPO₄ upon cycling also indicate small edge shift between fully charged and fully discharged samples [27].

From the above we confirmed that parameters of the synthesis used for LiCoPO₄ can be applied to obtain olivine phase of NaCoPO₄. Therefore electrochemical performance of NaCoPO₄ can be expected to be similar to the one obtained for LiCoPO₄ and can be further improved via the same routes used for LiCoPO₄ such as: coating the NaCoPO₄ by homogenous layer of carbon or doping the active material by transition metal [40]. Carbon could act as a reductor to avoid the formation of undesirable impurities, and on the other hand, carbon could act as a nucleating agent to decrease the particle size of the final material (shorter diffusion lengths and a larger electrode/electrolyte contact area) [41].

4. Conclusion

We have synthesized both LiCoPO₄ and NaCoPO₄ via rapid low-temperature MW-assisted solvothermal approach. Optimal synthesis parameters provided LiCoPO₄ with orthorhombic phase and Pnma space group, while NaCoPO₄ has two phases with different space groups (Pnma and P65) which are both expected to be electrochemically active. By means of X-ray diffraction and DFT calculations, we have analyzed the crystal structure for both materials and revealed that stoichiometry of Na in NaCoPO₄ is reduced due to the presence of Na vacancies in the material. The presence of Na vacancies is further supported by Co K-edge XANES which revealed the distortions in the local coordination of material. The presence of Na vacancies is further supported by Co K-edge XANES which revealed the distortions in the local coordination of material. The presence of Na vacancies is further supported by Co K-edge XANES which revealed the distortions in the local coordination of material. 

The calculated voltage for LiCoPO₄ is 4.6 V and does not vary much across the Li concentration in the cell, which is close to the experimental value of 4.8 V. The theoretical voltage for NaCoPO₄ is 4.48 V comparable with the experimental one, theoretical voltage for Li₀.₅Na₀.₅CoPO₄ is 4.9V.

Acknowledgements

The authors acknowledge the Deanship of Scientific Research at King Khalid University for funding this work through research groups program under grant number R.G.P.1/12/39. A.V.S. acknowledges a support from the RFBR for X-ray absorption measurements and analysis according to the research project No 17-02-01350/17.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jpcs.2019.109192.

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