Solid State Ionics 326 (2018) 145–149

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

First-principles identification of spinel $CaCo_2O_4$ as a promising cathode material for Ca-ion batteries

Zhongjuan Zhao[a], Jinpei Yao[a], Baozhen Sun[a,b,*], Shuying Zhong[a], Xueling Lei[a], Bo Xu[a], Chuying Ouyang[a]

[a] Department of Physics, Laboratory of Computational Materials Physics, Jiangxi Normal University, Nanchang 330022, China
[b] Optoelectronics and Communication Key Laboratory of Jiangxi Province, Jiangxi Normal University, Nanchang, Jiangxi 330022, China

ARTICLE INFO

Keywords:
Ca-ion battery
Cathode material
Spinel structure

ABSTRACT

The search for potential cathode materials is essential for the development of Ca-ion-based batteries, which are a cheap alternative to Li-ion batteries. In this work, we report a first-principles investigation into the feasibility of using spinel $CaCo_2O_4$ as a cathode for Ca-ion batteries. The results show that the spinel $CaCo_2O_4$ structure is stable, indicating that the synthesis of this compound should be feasible. The predicted voltage is consistently above 3.0 V at any Ca concentration, which is interesting for a cathode. Electronic structure analysis shows that the extracted spinel $Ca_xCo_2O_4$ compounds are metallic, which is indicative of good electronic conduction properties. The calculated activation energy barriers for Ca^{2+} migration are 0.58 and 0.22 eV at 100% Ca and 0% Ca concentrations, respectively, which suggest favorable electrode kinetics. Overall, the demonstrated structural stability, high average voltage, good electronic conductivity and excellent Ca^{2+} mobility highlight the promising potential of spinel $CaCo_2O_4$ as a cathode for Ca-ion batteries. The new fundamental insights presented here should stimulate further work on spinel $CaCo_2O_4$ cathodes for Ca-ion batteries.

1. Introduction

Lithium-ion batteries (LIBs) have been extensively used as energy storage devices in portable electronics [1–3]. Nevertheless, LIBs are approaching the theoretical limitation of electrode materials. In addition, the limited resources of lithium in nature make the use of LIBs expensive in the long term. These stern realities extremely hamper the pervasive deployment of LIBs. Therefore, the development of alternative battery concepts is of important significance.

Multivalent ion batteries have been, and continue to be, an effective strategy to overcome the cost and energy limitations of LIBs [4–9]. Multivalent ions, such as Be^{2+}, Mg^{2+}, Ca^{2+} and Al^{3+}, are the most interesting candidates because of their lightweight and small ionic radii. Be^{2+} can be excluded as a candidate for multivalent ion batteries due to its rarity and toxicity. Al- and Mg-ion batteries have serious issues in terms of finding suitable electrolytes. For instance, ionic liquids have been proposed, but these are expensive and corrosive substances. Among them, Ca-ion batteries are an especially attractive alternative due to the high theoretical volumetric capacity of the calcium metal anode [10]. Calcium may also provide advantages compared to magnesium due to its more negative reduction potential and larger radius, which may allow for faster diffusion. More importantly, calcium is abundant in the Earth's crust (5th most abundant element *vs.* 25th for Li) [9], which may decrease the cost of materials and guarantee supply even for multi-fold increases in the size of the energy storage market. However, batteries based on calcium have attracted little attention. The viability of metal electrodeposition [11] has only recently been achieved and a few studies on possible cathode materials started to appear in 2015–2016 [12–15]. At this early stage of Ca-ion technology, more attention is devoted to finding a high specific energy cathode material.

Spinel oxides with the general formula AB_2O_4 (where A is a multivalent cation and B is a transition metal cation) are excellent candidates for this study [16–18]. This is due to their mixed spinel structure and available multiple potential oxidation state. They have been widely investigated as positive electrode materials for rechargeable batteries. An example of a promising spinel oxide cathode is Mn_2O_4. For example, $LiMn_2O_4$ exhibits excellent performance as a cathode for Li intercalation with a voltage of 3–4 V *versus* Li metal [19]. $MgMn_2O_4$ is very appealing as a cathode for Mg-ion batteries, in which the activation energy barrier for Mg^{2+} migration is only 0.4 eV [20]. $CaMn_2O_4$ has also been reported as a rechargeable Ca-ion battery cathode. The

* Corresponding author at: Department of Physics, Laboratory of Computational Materials Physics, Jiangxi Normal University, Nanchang 330022, China.
E-mail address: bzsun1980@126.com (B. Sun).

https://doi.org/10.1016/j.ssi.2018.10.004
Received 8 June 2018; Received in revised form 30 September 2018; Accepted 4 October 2018

voltages of $CaMn_2O_4$ are ~0.2 V higher than those of $MgMn_2O_4$ (*versus* their corresponding metals) [15]. In addition to Mn_2O_4, cobalt-containing spinel oxides, such as $NiCo_2O_4$ [21], $ZnCo_2O_4$ [22], $MnCo_2O_4$ [23], $CuCo_2O_4$ [24], and $MgCo_2O_4$ [25], are alternative promising oxide cathodes. They are technologically intriguing materials and have been studied as electrode materials for supercapacitor applications. Based on the above fact, spinel $CaCo_2O_4$ can also be expected to exhibit both reasonable Ca-ion diffusion and high energy density. In fact, Cabello et al. [14] originally utilized $CaCo_2O_4$ as a cathode material for Ca-ion batteries. However, their investigated $CaCo_2O_4$ is monoclinic (P2/m space group), not spinel structure. Compared to monoclinic $CaCo_2O_4$, the spinel structure offers a three-dimensional channel for the transport of Ca^{2+} ions. For this purpose, we decided to explore the novel use of spinel $CaCo_2O_4$ as a cathode for Ca-ion batteries.

First-principles calculations have achieved great success in understanding or predicting the physical and chemical properties of electrode materials [26,27]. Herein, we present a first-principles investigation on the electronic and electrochemical properties of spinel $CaCo_2O_4$, aiming to predict the possibility of spinel $CaCo_2O_4$ as a cathode for Ca-ion batteries. Specifically, we calculated the voltage curve for Ca (de)intercalation and the paths and barriers for Ca-ion diffusion at different concentrations in the spinel $Ca_xCo_2O_4$ (x = 0, 0.25, 0.5, 0.75 or 1) structure. The present theoretical investigation serves to gain broader insights to advance the search for Ca-based cathode materials.

2. Computational details

First-principles calculations were performed using the Vienna *Ab Initio* Simulation package (VASP) [28] within the projector augmented-wave (PAW) approach [29]. The plane-wave cutoff energy was 550 eV and the Brillouin zone was sampled with a 3 × 3 × 3 *k*-point set. Exchange-correlation effects were described with the general gradient approximation (GGA) and the Perdew, Burke and Ernzerhof (PBE) functional [30]. The GGA + *U* methodology was used to account for the metal d-orbitals with an effective Hubbard $U_{eff} = U - J = 3.9$ eV (J = 1.00 eV) for Co atoms, which are based on previous references [31] and our tests. Gaussian smearing with a smearing factor of 0.05 eV was used in all calculations. The total energy was converged within 10^{-5} eV per formula unit. The optimized structures were obtained by relaxing all atomic positions and lattice vectors until forces were smaller than 0.01 eV/Å. Spin polarized calculations were performed in all cases. Ca^{2+} migration in spinel $CaCo_2O_4$ was investigated using the nudged elastic band method (NEB) [32], which is an effective approach to search for the transition state.

Phonon dispersion was calculated using the supercell (112 atoms) force constant method. The harmonic second order interatomic force constants (IFCs) were obtained within the linear response framework by employing the density functional perturbation theory (DFPT) [33], as supplemented in VASP. We could then obtain the phonon dispersion of spinel $CaCo_2O_4$ using the PHONOPY [34] package based on the harmonic second order IFCs.

3. Results and discussion

3.1. Crystal structure of spinel $CaCo_2O_4$

We first examined the stability of the $CaCo_2O_4$ spinel structure. Calculations of vibrational frequencies may reveal structural instabilities through low or imaginary phonon frequencies. Therefore, phonon dispersion could give a criterion for the crystal stability by the prediction of soft modes, such as $SrTiO_3$ [35]. If all phonon frequencies are positive, the crystal is stable. If some frequencies are imaginary (soft modes), then the system is unstable. The calculated phonon dispersion curves of spinel $CaCo_2O_4$ (*FD-3MS* space group) along several high symmetry lines in the first Brillouin zone are plotted in Fig. 1. No soft modes are observed in the phonon dispersion curves, suggesting this structure is dynamically stable. On the other hand, we also calculated the formation energies for the decomposition of $Ca_xCo_2O_4$ (x = 0.25, 0.5, 0.75, and 1) into $Ca_2Co_3O_8$, CaO, and Co_3O_4. The calculated results are listed in Table 1. These results indicate the spinel-$Ca_xCo_2O_4$ (x = 0.25, 0.5, 0.75, and 1) may happen the decomposition reaction listed in Table 1 thermodynamically. Of course, they are also dissociated into other products. The formation energy for the decomposition reaction of $CaCo_2O_4$ is just −0.05 eV/atom. Obviously, the energy above the energy convex hull is not too high. This indicates it is feasible for the use of spinel $CaCo_2O_4$ as a cathode material. In comparison with $CaCo_2O_4$, $Ca_xCo_2O_4$ (x = 0.25, 0.5, and 0.75) compounds are easier to happen decomposition reaction. In fact, we know many cathode materials are not global stable during electrochemical reaction. $LiCoO_2$ is a typical example, as Li_xCoO_2 (when x < 0.5) can be dissociated into Co_3O_4 under high temperatures [36]. However, $LiCoO_2$ is still the most commonly used material for Li-ion batteries. Similarly, we think spinel-$CaCo_2O_4$ may also be used as a cathode for Ca-ion batteries. Therefore, the spinel structure, as shown in Fig. 2, was chosen to model the $CaCo_2O_4$ crystal in our calculations. It is composed of Ca^{2+} occupying tetrahedral 8*a* sites (purple polyhedra in Fig. 2(a)) and Co^{3+} occupying the octahedral 16*d* sites (yellow polyhedra in Fig. 2(a)) within a cubic close-paced O^{2-} lattice. Our investigated structure contains 8 Ca, 16 Co and 32 O atoms. The structure was relaxed in both lattice parameters and atomic positions. The optimized cell parameters were determined to be $a = b = c = 8.51$ Å.

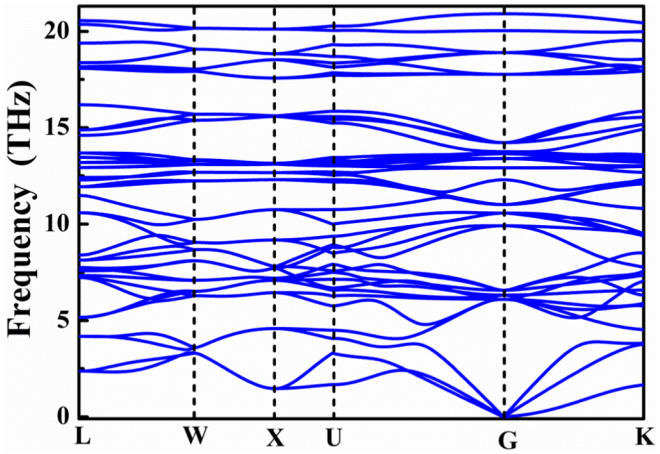

Fig. 1. Phonon dispersion of spinel $CaCo_2O_4$. L, W, X, U, G and K are (0.5 0.5 0.5), (0.5 0.25 0.75), (0.5 0 0.5), (0.625 0.25 0.625), (0 0 0) and (0.75 0.375 0.375) high symmetry points, respectively.

Table 1
Formation energies (E_f) for the decomposition reaction of $Ca_xCo_2O_4$.

Decomposition reaction	E_f (eV/atom)
$6CaCo_2O_4 = Ca_2Co_3O_8 + 3Co_3O_4 + 4CaO$	−0.05
$24Ca_{0.75}Co_2O_4 = 6Ca_2Co_3O_8 + 10Co_3O_4 + 6CaO + O_2$	−0.09
$12Ca_{0.5}Co_2O_4 = 2Ca_2Co_3O_8 + 6Co_3O_4 + 2CaO + 3O_2$	−0.21
$24Ca_{0.25}Co_2O_4 = 2Ca_2Co_3O_8 + 14Co_3O_4 + 2CaO + 11O_2$	−0.20

3.2. Average voltage and volume changes

One challenge to overcome when developing new cathode materials for Ca-ion batteries is to establish an adequate operating voltage (in the range of ~2.0–3.0 V). Based on the stable $Ca_xCo_2O_4$ configurations, we can calculate the average (de)intercalation potential as a function of concentration. The voltage (*V*) was calculated as: [37]

$$V = -\frac{E(x_2) - E(x_1) - (x_2 - x_1)E(Ca^{bulk})}{z(x_2 - x_1)} \quad (1)$$