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Computational and experimental understanding of Al-doped $Na_3V_{2-x}Al_x(PO_4)_3$ cathode material for sodium ion batteries: Electronic structure, ion dynamics and electrochemical properties

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ABSTRACT

First principles calculations are employed to understand the effects of Al substitution on the electronic structure, ion dynamics properties, as well as structural stability of $Na_3V_{2-x}Al_x(PO_4)_3$ cathode material. The results reveal that Al doping decreases the band gap energy and transforms the material from indirect to direct band gap electronic structure. Several Na-ion diffusion routes in the crystal structure are proposed and the one with lowest migration energy is identified, which shows one-dimensional transport characteristics along *c*-axis direction via a curved trajectory. The Al doping increases the Na ion migration energy and thus unfavorable for Na ion diffusion in the crystal. The opposite effects of Al doping on electronic and Na ionic conduction lead to the occurrence of an optimal Al doping level, at which the best electrode reaction kinetics can be expected. The experimental works of the synthesized $Na_3V_{2-x}Al_x(PO_4)_3$ with $x = 0–0.4$ confirm the theoretical predictions. The sample $Na_3V_{1.8}Al_{0.2}(PO_4)_3$ with appropriate Al doping exhibits the smallest electrode polarization and superior rate performance. Because of the enhanced binding energy with Al doping as indicated by computation work, the $Na_3V_{1.8}Al_{0.2}(PO_4)_3$ material displays much stable long-term cycling performance compared to the pristine sample at different temperatures.

1. Introduction

Recently, sodium-ion batteries (NIBs) have attracted considerable attention as a promising alternative to lithium-ion batteries (LIBs), especially considering large-scale grid balancing issues related to an integration of intermittent renewables. NIBs are also considered as a suitable power source for various types of (bigger size) electric vehicles. This is due to its lower cost, improved safety, abundant raw material and wide distribution of sodium [1–3]. Furthermore, a rather close similarity of Na and Li in respect to the chemical properties is expected to accelerate the development of NIBs technology and facilitate the replacement of LIBs in the mentioned applications [4–6]. Theoretically speaking, NIBs are not expected to reach the energy density of LIBs, because of a lower standard electrochemical potential and a heavier atomic mass of Na than Li. However, with a progress in designing of novel, excellent electrode materials with an improved storage capacity and cyclability, technology of sodium batteries should quickly achieve mature status, with a dynamically increasing range of commercial applications and quickly growing market.

Currently, various cathode materials, which can be categorized into two main groups of oxides (e.g. Na_xMO_2 [7–10] where M - selected 3d metal, V_2O_5 [11,12]) and polyanion-based compounds (e.g. $NaMPO_4$ [13,14], Na_2FePO_4F [15], $NaVOPO_4$ [16], $Na_3M_2(PO_4)_2F_3$ [17,18]), have been extensively studied. Among those candidates, Na Super-Ionic Conductor (NASICON)-type $Na_3V_2(PO_4)_3$,

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abbreviated here as NVP, is known for a high sodium ionic conductivity [19,20], high thermal and chemical stability [21], as well as good electrochemical properties, and therefore is of a particular interest [22–24]. It should be noticed that possibility for a rapid Na^+ diffusivity in NVP can be associated with an intrinsic presence of 3D open diffusion pathways, with reported diffusion coefficient for sodium transport exceeding 10^{-11} cm^2 s^{-1} at room temperature [25,26]. Such value is at least several orders of magnitude larger than that for many other candidate NIBs cathodes (ca. 10^{-14} cm^2 s^{-1} for $NaMn_3O_5$ [27], 10^{-17} cm^2 s^{-1} for $NaFePO_4$ [14]). More importantly, with a remarkable theoretical capacity of 117.6 mA h g^{-1} (theoretical value corresponding to two Na cations extraction per unit formula) and a high voltage plateau of 3.4 V versus Na / Na^+ electrode, the material gravimetric energy density can reach as high as 401 W h kg^{-1} [28,29].

All of the above listed advantages make NVP a promising cathode material for NIBs. However, the compound suffers from low electronic conductivity, which can severely limit its electrode reaction kinetics and therefore rate capability. The poor electronic conductivity is characteristics of the phosphate materials and associated with structural constrains of the NASICON framework. In the crystal structure of $Na_3V_2(PO_4)_3$, vanadium-containing octahedra are isolated and only interlinked via PO_4 tetrahedra, which limits the transmission of electrons via a small polaron mechanism. As a result, the electrochemical performance of the NVP is strongly limited, especially in respect of the rate capability. For example, Jian et al. reported about NVP synthesized by solid state reaction, which delivered only 29 mA h g^{-1} at 1 C [30]. In another report for NVP prepared via a polyol-assisted pyro-synthetic reaction, Kang et al. measured capacity of 65 mA h g^{-1} at 2.67 C [31]. It is therefore clear that the reported so far electrochemical performance of pristine NVP is rather not encouraging, and hence, more systematic explorations to improve the electronic conductivity and rate performance of NVP-based electrodes for NIBs are urgently needed.

Until now various strategies have been undertaken to increase the electronic transport kinetics of NVP-based cathodes, in order to enhance the sodium storage performance [32–34]. From one side, coating of the active particles with conductive materials, reduction of the size down to nanoscale and modification of the synthesis procedure to obtain special morphology of the powder particles have been proposed, but also doping of the parent $Na_3V_2(PO_4)_3$ with different ions, especially at the vanadium site, has been considered. In such case of chemical substitution, V^{3+} has been reported to partially substitute by aliovalent Mg, Ni and Mn as well as by isovalent Al, Cr and Fe ions to improve the electrochemical performance. Among the substituent ions, particularly Al^{3+} has shown to be an effective dopant for the lithium- and sodium-based NASICON phases, concerning enhancement of the electrochemical properties [35–39]. For example, an improvement of ionic conductivity of $Li_{1+x}Ti_{2-x}Al_x(PO_4)_3$ compounds has been demonstrated by Mouahid et al. which was related to a higher charge carrier concentration appearing when small amount of Ti^{4+} was replaced for Al^{3+} [35]. Lu et al. reported the Al-doped $Li_3V_{1.9}Al_{0.1}(PO_4)_3$ material, which exhibited a higher reversible capacity of 70 mA h g^{-1}, compared to only 15 mA h g^{-1} for the undoped $Li_3V_2(PO_4)_3$ at 5 C rate [37]. From the crystal chemistry point of view, Lalère et al. investigated the structural changes upon extraction/insertion of Na^+ from/into $Na_3V_{2-x}Al_x(PO_4)_3$, and they demonstrated that Al doping increases remarkably the energy density of NVP electrodes (up to 425 Wh kg^{-1}), due to the lighter molecular weight of Al and the V^{4+}/V^{5+} redox couple at 3.95 V [38]. Recently, Aragón et al. reported that the Al doping can significantly enhance the rate performance of NVP, 96.8 mAh g^{-1} at 6 C was achieved by $Na_3V_{1.8}Al_{0.2}(PO_4)_3$ sample [39]. However, excessive Al doping (higher than 0.2) does not lead to the expected further improvement of the electrochemical performance. Although the work by Sanz et al. showed that the Li ion mobility is higher in Al-doped $Li_3Ti_{1.8}Al_{0.2}(PO_4)_3$ than in the pristine one [40,41], the effect of Al doping on the Na ion and electron transport of $Na_3V_2(PO_4)_3$ is unknown. The substitution of Al for V is not expected to produce any charge defects considering their isovalent feature from defect chemistry point of view. While, the Aragón's work [39] and our results shown below revealed that Al doping for V really has positive influence on the electrochemical property improvement. Understanding of the behind reasons, especially the intrinsic electronic structure change with Al doping, is crucial to the optimization of electrochemical performance of NVP and design of new chemistry system.

To our best knowledge, there is no reports so far about the DFT calculation of electronic structure of the Al-doped NVP and no attempt has been made to understand the action mechanism of Al dopant in NVP crystal. In this work, we conduct theoretically and experimentally investigation of the effects of Al doping on the physical properties and electrochemical performance of NVP with the aim of better elucidation of the correlation between structure and properties.

2. Theoretical calculation and experimental

2.1. First principles calculations

In order to explore effects of Al doping on the electronic structure and ion dynamics of the considered materials, the total energy, density of states (DOS) and Na-ion migration energy barriers for the undoped and doped NVP were calculated through Cambridge Serial Total Energy Package (CASTEP) function implemented in Materials Studio (MS) software [42,43]. In the performed calculations, the exchange-correlation potential, based on generalized gradient approximation (GGA) and the Perdew-Burke-Ernzerhof (PBE) scheme, was used. A Hubbard-type correction U, which was set as 4.0 eV for vanadium [21,44], was employed to eliminate the strongly correlated effect of the 3d electrons. No U correction was considered for other atoms. The cut-off energy of the plane waves was chosen at 330 eV and the Brillouin zone integrations were approximated using a special $1 \times 3 \times 3$ k-point sampling scheme of Monkhorst-Pack for the unit cell. Geometry optimizations were performed by an iterative process, using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm in order to minimize the energy with respect to the atomic positions. The convergence condition of the residual force was set at 10^{-6} eV/atom. The calculations were performed in a unit cell consisting of 4 formula units of $Na_3V_2(PO_4)_3$ (Fig. S1). To study the Na-ion diffusion in $Na_3V_2(PO_4)_3$, we considered all possible Na vacancy arrangements within the unit cell. Among them, we picked up Na vacancy arrangement with the lowest energy through the geometry optimization method and then calculated their energies with GGA + U. The sodium vacancy conformation used in our model is in accordance with other reported literatures [45,46]. The energy of $Na_3V_{1.75}Al_{0.25}(PO_4)_3$ with Al-substitution in different positions were also calculated, and the lowest energy structures were selected for further considerations. It should be mentioned that the selection of doping amount 0.25 in $Na_3V_{1.75}Al_{0.25}(PO_4)_3$ is to simulate the experimental $Na_3V_{1.8}Al_{0.2}(PO_4)_3$ composition and at the same time to simplify the calculation process. Possible diffusion pathways of sodium ions were determined by analyzing the elementary diffusion routes and calculating the corresponding migration energy barriers using the transition state search (TS Search) method [47,48]. The route with lowest migration energy is considered.