

Towards polyvalent ion batteries: A zinc-ion battery based on NASICON structured $\text{Na}_3\text{V}_2(\text{PO}_4)_3$

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ABSTRACT

Zinc-ion batteries are considered as potential large-scale renewable energy storage devices due to low redox potential, low cost, large capacity, high electric conductivity, nontoxicity and easy processing of zinc metal. However, the development of cathode materials for zinc-ion batteries to date has been mainly limited to tunnel manganese oxides and Prussian blue analogues. Here we have firstly developed NASICON structured $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ as cathode material for Zn-ion batteries. To compensate the low conductivity, graphene-like carbon wrapped $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ nanoparticles are fabricated. With $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ as cathode, Zn metal as both counter and reference electrodes, and $0.5 \text{ mol L}^{-1} \text{ Zn}(\text{CH}_3\text{COO})_2$ solution as electrolyte, the aqueous Zn-ion battery delivers a reversible capacity of 97 mA h g^{-1} at 0.5 C and retains 74% capacity after 100 cycles. Meanwhile, the battery can be charged and discharged at high rate up to 10 C . The cyclic voltammogram analysis shows that the Zn-ion storage in $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ is a diffusion-controlled kinetic process. A mechanism of Zn ion occupancy variation during cycling is proposed. Our results provide an example for understanding and designing the intercalation process of divalent metal ions in NASICON structured cathode for new type rechargeable divalent metal ion batteries.

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1. Introduction

With increasing stress on environmental pollution and energy shortage, pursuit for new energy storage technologies with high performance, safety and eco-friendliness are becoming more and more urgent [1–3]. In recent years, the rechargeable batteries based on multivalent metal anodes have received much interest, such as Zn, Mg, Al, etc. These metal-based anodes show very high energy density (Zn: $5851 \text{ mA h mL}^{-1}$; Mg: $3833 \text{ mA h mL}^{-1}$; Al: $8046 \text{ mA h mL}^{-1}$) [4–6], among which Zn anode is more suitable for practical application in aqueous system due to higher redox potential of -0.78 V vs. standard hydrogen electrode (SHE). Considering its low redox potential, low cost, large capacity, high

electric conductivity, nontoxicity and easy processing, zinc metal is an ideal anode to develop high energy density aqueous system batteries, *i.e.*, Zn-ion batteries (ZIBs).

Up to now, only a few cathode materials have been reported as intercalation hosts for divalent Zn^{2+} ions. Tunnel-type manganese oxides have been mostly investigated [7–13]. Kang and coworkers [7] have explored α -, β -, γ -, and δ -types MnO_2 with different tunnel structures as intercalation hosts for Zn^{2+} , and found that α -type MnO_2 with 2×2 tunnel exhibits excellent electrochemical performance. Lee et al. [8,9] observed a reversible phase transition of α - MnO_2 from tunneled to layered polymorphs during charge/discharge process, but the repeated phase transitions lead to an excessive structural stress that may result in the gradual conversion to amorphous phase and hence capacity decay at high rates. Recently, a 3×3 tunnel todorokite-type MnO_2 with improved cyclic stability were reported [10]. The intercalation mechanisms of Zn^{2+} into spinel γ - MnO_2 and phase transitions during cycling were also systematically investigated [11]. Prussian blue analogues are the other kind of attractive cathode materials for ZIBs [14]. Liu and coworkers [14] developed a zinc hexacyanoferrate (ZnHCF)

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cathode for aqueous ZIBs with energy density up to 100 W h kg^{-1} . Trocoli et al. [15] developed a ZIB based on CuHCF via a similar route. Besides, there are some hybrid aqueous systems based on Zn anode, in which the cathode materials are actually those used in lithium or sodium ion batteries [16–21].

Since the radius of Zn^{2+} ion is 0.74 \AA which is smaller than Na^+ ion (0.99 \AA), volume variation during Zn^{2+} insertion would be small if the cation radius is the only factor under consideration [22]. However, high polarization of Zn^{2+} ion may limit its migration dynamics [4]. Tunnel manganese oxides and Prussian blue analogues are the only two families that have been reported as Zn^{2+} intercalation cathode materials. In this work, we focus our interest on the NASICON $\text{A}_x\text{MM}'(\text{XO}_4)_3$ ($\text{A}=\text{Li}, \text{Na}, \text{Mg}, \text{etc.}$, $\text{M}, \text{M}'=\text{Ti}, \text{V}, \text{Cr}, \text{Fe}, \text{etc.}$, $\text{X}=\text{P}, \text{Si}, \text{S}, \text{etc.}$) compounds. This large family of polyanionic cathode materials own very stable framework that is favorable for long cycle; the redox voltage is higher than the binary oxide analogue due to the inducing effect; plenty of vacancies existing in the structure can store metal ions [23]. Many studies took $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ as cathode for monovalent metal ions such as Li and Na ions [24–32]. However, to the best of our knowledge, no attempts have been made to use $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ as intercalation cathode for divalent metal ions such as Zn^{2+} , Mg^{2+} and Ni^{2+} ions. The Zn^{2+} , Mg^{2+} and Ni^{2+} ions possess smaller radii of 0.74 , 0.72 and 0.69 \AA , respectively, as compared with Na^+ cation [22], indicative of a possible application as guest species stored in the framework. In this work, graphene-like carbon wrapped $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ was fabricated to validate the divalent metal ion storage behavior in these compounds. This is the first time to use $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ as intercalation host for divalent cations. A new and eco-friendly Zn-ion battery was designed by using $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ as cathode, zinc as anode and $\text{Zn}(\text{CH}_3\text{COOH})_2$ as aqueous electrolyte, as shown in Fig. 1a. The electrochemical

performances and intercalation mechanisms of Zn-ions were demonstrated.

2. Experimental section

The NASICON structured NVP nanoparticles wrapped by graphene-like carbon were obtained via hydrothermal route followed by post calcination. In a typical process, $2 \text{ mmol V}_2\text{O}_5$, $6 \text{ mmol NH}_4\text{H}_2\text{PO}_4$ and $3 \text{ mmol Na}_2\text{CO}_3$ were mixed in 35 mL distilled water under vigorous stirring at room temperature. Then, 6 mmol citric acid and 3 mL polyethylene glycol 400 (PEG-400) were added to form a blue suspension. The suspension was stirred for 2 h and then transferred to a 50 mL Teflon-lined autoclave. The autoclave was sealed and kept at $180 \text{ }^\circ\text{C}$ for 48 h , and then naturally cooled down to room temperature. The resulting brown mixture was ultrasonically treated for 90 min to form a uniform dispersion, and then dried at $120 \text{ }^\circ\text{C}$ for 24 h . Under protection of N_2 flow, the dried powder was first heated at $350 \text{ }^\circ\text{C}$ for 5 h , then ground, and finally sintered at $750 \text{ }^\circ\text{C}$ for another 8 h .

The battery was assembled in a breaker. Blends of active material, acetylene black and PVDF in a mass ratio of $8:1:1$ were fully mixed, pasted on nickel foam strips. After drying at $80 \text{ }^\circ\text{C}$ overnight in an oven, the strips were tested in a breaker by using $0.5 \text{ mol L}^{-1} \text{ Zn}(\text{CH}_3\text{COO})_2$ solution as the electrolyte and Zn metal as both counter and reference electrodes. The cycling tests were carried out on battery testing system (LAND, China) at a voltage range of $0.8\text{--}1.7 \text{ V}$, from 0.5 to 10 C ($1 \text{ C}=100 \text{ mA g}^{-1}$) at $25 \text{ }^\circ\text{C}$. Cyclic voltammogram (CV) tests were performed on electrochemistry workstation (PARSTAT 2273, US). The sodium storage electrochemical performance in organic electrolyte was measured in $1 \text{ mol L}^{-1} \text{ NaClO}_4$ solution of propylene carbonate/ethyl

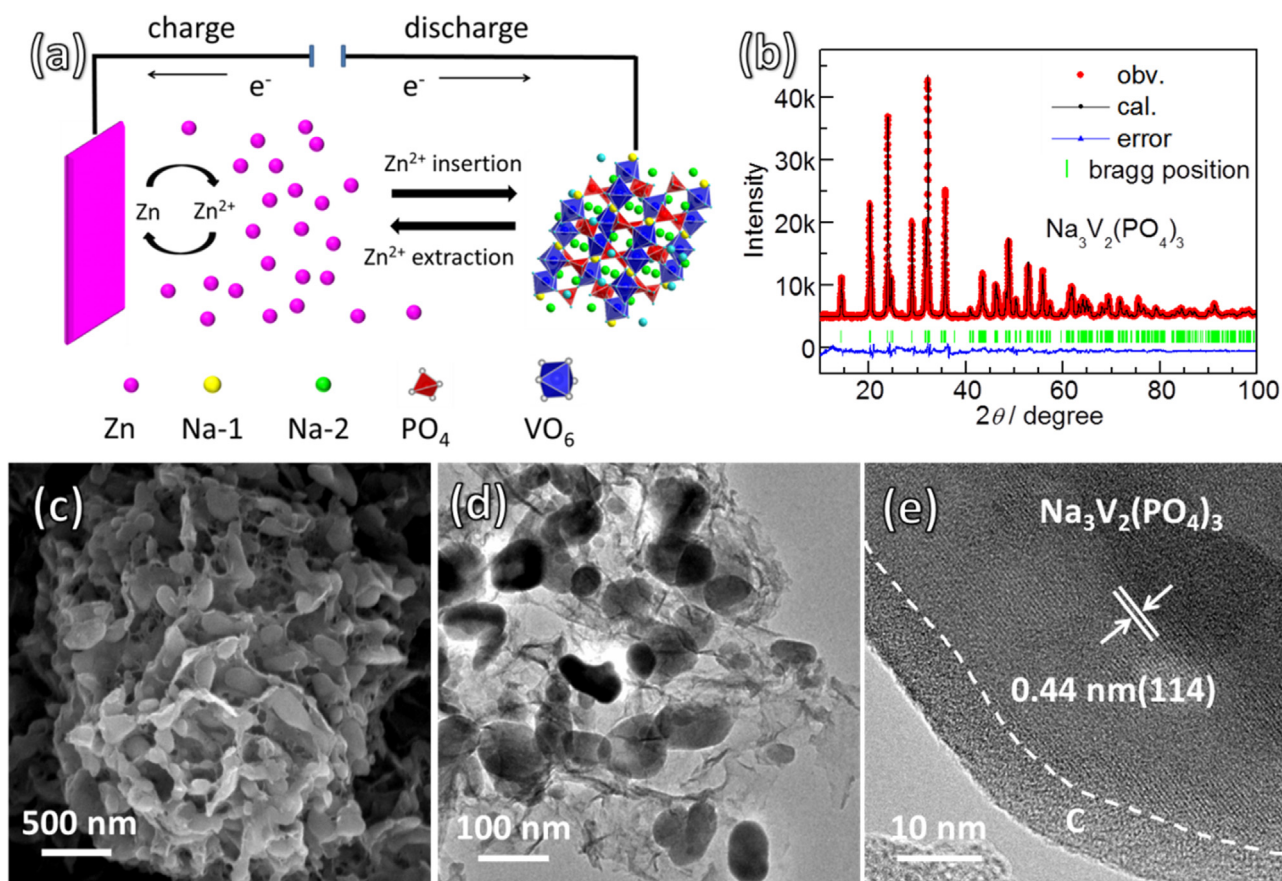


Fig. 1. (a) Schematic illustration of Zn- $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ aqueous rechargeable battery; (b) Rietveld-refined XRD pattern, (c, d) SEM and (e) TEM image for $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ sample.

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