IOP Publishing | Songshan Lake Materials Laboratory

Mater. Futures 2 (2023) 023502 (14pp)

Perspective

Materials Futures

https://doi.org/10.1088/2752-5724/acc7bb



Unlocking the multi-electron transfer reaction in NASICON-type cathode materials

Yuan Liu^{1,2} Xiaohui Rong^{1,2,3,*}, Fei Xie¹, Yaxiang Lu^{1,4}, Junmei Zhao^{5,*}, Liguan Chen

and Yong-Sheng Hu^{1,2,3,4}

¹ Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

² College of Materials Science and Optoelectronic Technology, University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

³ Yangtze River Delta Physics Research Center Co. Ltd, Liyang 213300, People's Republic of China ⁴ Huairou Division, Institute of Physics, Chinese Academy of Sciences, Beijing 101400, People's Republic of China

⁵ CAS Key Laboratory of Green Process and Engineering, State Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing, People's Republic of China *É-mail: rong@iphy.ac.cn* and

jmzhao@ipe.ac.cn

Abstract

The growing concern about scarcity and large-scale applications of lithium resources has attracted efforts to realize cost-effective phosphate-based cathode materials for next-generation Na-ion batteries (NIBs). In previous work, a series of materials (such as Na₄Fe₃(PO₄)₂(P₂O₇), Na₃VCr(PO₄)₃, Na₄VMn(PO₄)₃, Na₃MnTi(PO₄)₃, Na₃MnZr(PO₄)₃, etc) with \sim 120 mAh g⁻¹ specific capacity and high operating potential has been proposed. However, the mass ratio of the total transition metal in the above compounds is only ~ 22 wt%, which means that one-electron transfer for each transition metal shows a limited capacity (the mass ratio of Fe is 35.4 wt% in LiFePO₄). Therefore, a multi-electron transfer reaction is necessary to catch up to or go beyond the electrochemical performance of LiFePO₄. This review summarizes the reported NASICON-type and other phosphate-based cathode materials. On the basis of the aforementioned experimental results, we pinpoint the multi-electron behavior of transition metals and shed light on designing rules for developing high-capacity cathodes in NIBs.

Keywords: NASICON, Na-ion batteries, cathode materials, multi-electron transfer reactions

1. Introduction

Large-scale applications based on Na-ion batteries (NIBs) are expected to integrate intermittent renewable energy sources because of the low cost, wide distribution, and abundant reserves of sodium resources [1-7], where the development of electrode materials is one of the most significant tasks for the improvement of NIBs. In terms of cathode materials, polyanion compounds have high safety and chemical/electrochemical stability [8], which could match the urgent requirement of grid energy storage devices. Among the phosphate-based cathodes, NASICON-type materials have attracted growing attention due to their high Na^+ ion conductivity [9–12]. It took 30 years from identifying the crystal structure to realizing reversible charge/discharge behavior in the NIBs (figure 1(a)). As early as 1968, Hagman's group [13] reported the Na $Me_2(PO_4)_3$ (Me = Ge, Ti, Zr) structure. They mentioned that the crystal's 3D framework is built up of the corner link of MeO_6 octahedra and PO_4 tetrahedra, and the oxygen atoms octahedrally surround the sodium atoms. In 1976, Goodenough and Hong et al [14, 15] found fast alkali-ion transport in a series of materials conforming to the chemical formula Na_{1 + x}Zr₂P_{3-x}Si_xO₁₂($0 \le x \le 3$). These compounds were

* Authors to whom any correspondence should be addressed.

1



Original content from this work may be used under the terms of the Creative Commons Attribution 4.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.



Perspective

(a) Theoretical and practical milestones in phosphate-based compounds for Na-ion batteries (NIBs).





Figure 1. (a) Timeline of the development of phosphate-based cathode materials. (b) Potential and specific capacity of different cathode materials. Squares are one-electron reactions of each transition metal (named $1e^{-}/TM$); the circle symbols are $1.5e^{-}/TM$. NOTE: the reactions with $1.5e^{-}/TM$ in Na₄VMn(PO₄)₃ and Na₄VFe(PO₄)₃ are irreversible.

named NASICON (sodium (Na) super (S) ion (I) conductor (CON)), benefiting from the three-dimensional diffusion tunnel. Subsequently, Nadiri *et al* [16] used Fe₂(MoO₄)₃ for the positive electrode and $ACIO_4$ (1 M, A = Li/Na) in propylene carbonate as the electrolyte to fabricate half cells, revealing the intercalation behavior of alkali metal ions in the NASICON framework. In 1988, reversible electrochemical (de)intercalation was successfully realized in $ATi_2(PO_4)_3$ for the first time [17]. However, much research focused on LIB material systems after the first commercial lithium-ion battery was issued in 1991. In 2002, Uebou *et al* reported electrochemical sodium insertion/extraction of the 3D framework of Na₃V₂(PO₄)₃ [18], which was synthesized by Delmas in 1978 [19]. However, the insufficient electrochemical data attracted limited attention to such materials until Hu's group first proposed the carbon coating approach to significantly improve the cycling and rate performance [20].

Since then, $Na_3V_2(PO_4)_3$ has been regarded as a promising cathode candidate earning wide investigation, and several modification strategies have been explored to optimize its electrochemical performance [20–22]. However, vanadium's high cost and low resource sustainability became one of the most serious bottlenecks contrary to the requirements of large-scale applications [23]. In 2013, Hu's group proposed $Mn^{2+/3+/4+}$ redox couples in NASICON-type cathodes, and kinds of Mn-rich compounds were designed (such as $Na_3MnTi(PO_4)_3$ and Na₃MnZr(PO₄)₃, etc) [24]. Subsequently, the reversible redox couples of $Mn^{2+/3+/4+}$ in a NASICON-type cathode have been realized with a high operating potential in Na₃MnTi(PO₄)₃ (~3.6 V and ~4.0 V) [25]. Furthermore, Fe-rich NASICON-type cathode materials (such as Na₃Fe₂(PO₄)₃) have attracted great interest due to their wide sources, low costs and abundant reserves on Earth. However, the limited thermodynamic equilibrium potential of Fe^{2+/3+} restricted the research of Fe-based NASICON-type cathodes. It is exciting that researchers found that P₂O₇⁴⁻ and F⁻ can increase the redox potential based on Fe^{2+/3+} due to the strong electronegativity of such ions. As a result, a series of new structures has been discovered for phosphate-based mixed-polyanion cathodes [26–28]. However, the low transition metal mass fraction of the above compounds leads to a limited theoretical specific capacity, as shown in figure 1(b). Therefore, realizing the multi-electron transfer reaction is crucial for advanced next-generation NIBs.

In this review, we summarized redox couples with electrochemical activity in NASICON-type cathodes and other polyanionic compounds. Based on reported voltage profiles and previous accumulations on multi-electron transfer reactions, we pinpoint the reversibility of redox couples in NASICON-type cathodes closely related to the crystal structure. As a result, we demonstrate a cascade of guiding lines for enabling better designs of high-capacity polyanionic NIB cathodes.

2. Structure

NASICON-type cathode materials are increasingly attracting attention as phosphate-based compounds due to tunable transition metal sites and fast Na⁺ ion transport pathways. As early as 1976, a series of materials with the chemical formula Na_{1+x}Zr₂P_{3-x}Si_xO₁₂($0 \le x \le 3$) were named NASICON (an acronym for sodium (Na) Super Ionic CONductor) [14]. Similarly, NASICON-type material structures usually refer to a family of solids with the chemical formula AMM'(PO_4)₃ [11]. Where the 'A' site can be occupied by alkali ions (Li⁺, Na⁺, K^+ , Rb^+ , and Cs^+), alkaline earth ions (Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+}), transition metals (Cu^{2+} , Ag^+ , Pb^{2+} , Cd^{2+} , Mn^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Al^{3+} , Ge^{4+} , Zr^{4+} , and Hf^{4+}), and ion-molecules (H_3O^+ and NH_4^+), may also be vacancies. The M and M' sites are divided by 3d (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn), 4d (Y, Zr, Nb, Mo), 5d (Lu, Hf, Ta), and main-group (Al, Si, In, Ge, As, Sn, Sb) elements to balance the charge appropriately. Phosphorus can be partially or even entirely replaced by S, Si, As, W and Mo, while O can also be replaced by F and Cl. Furthermore, the crystal structure can be rhombohedral, monoclinic, triclinic, orthorhombic, garnet, SW-type, corundum, etc, with different elements. Notably, rhombohedral structures have been extensively reported due to their superior ion diffusion pathway. In this structure, MO₆ and M'O₆ octahedrons share all angles with XO₄ tetrahedrons, and MO₆ and M'O6 octahedrons are arranged linearly along the c-axis. The octahedron MO₆ and M'O₆ connect three tetrahedral XO₄ units to form a basic unit called a lantern [29]. Each lantern is connected to six other lanterns, thereby constructing a stable 3D skeleton structure [30]. In this open 3D framework, interconnected channels provide a high-speed transmission pathway for the ions encapsulated in the 'A' site. Intriguingly, its content is between 1 and 5 [31, 32]. In addition, it can be de-intercalated continuously without structural collapse.

3. Electrochemical performance of reported materials

The NASICON-type compounds are much favored by the open 3D diffusion channels and stable skeleton structure. Currently, research focuses on the following directions: optimizing strategies for $Na_3V_2(PO_4)_3$ -based materials (e.g. carbon coating [20, 33–37], morphology control [22, 38], element doping

[21, 39–45], etc), and exploring unknown material systems by replacing the M/M' transition metal sites [25, 46–48]. To date, the NASICON-type cathode materials with various electrochemically active metals (V, Mn, Fe, Cr, Ti, etc) have been extensively explored. Meanwhile, phosphate-based mixed-polyanion compounds (such as $Na_3V_2(PO_4)_2F_3$, $Na_4Fe_3(PO_4)_2(P_2O_7)$, Na_2FePO_4F , etc) have also been proposed as cathodes in NIBs.

3.1. V-based NASICON cathodes

Vanadium compounds have attracted great attention for their excellent redox, electrochemical, catalytic, and magnetic properties [49–51]. Surprisingly, the vanadium atoms can adopt different oxidation states (from II to V), coordination (from 6 to 4), and environments (octahedral to tetrahedral) in the reported vanadium phosphates. Abundant bonds lead to a wide variety of V-based polyanion compounds. Na₃V₂(PO₄)₃ can be indexed as the rhombohedral phase $R\bar{3}C$ space group [29, 32, 52], and the oxidation state of V in Na₃V₂(PO₄)₃ is confirmed to be trivalent [31]. As a cathode material, it exhibits a theoretical specific capacity of 117.6 mAh g⁻¹ with 3.4 V operating voltage (vs. Na⁺/Na). The incompletely occupied Na⁺ sites provide a fast ion diffusion channel, which enables the material to exhibit excellent rate capability [53]. Furthermore, Masquelier *et al* have made many contributions to elucidate the crystal structure and charge/discharge behavior of Na₃V₂(PO₄)₃ [32, 52].

The transition metal substitution of the V element in $Na_3V_2(PO_4)_3$ has also been widely studied due to the high cost of V-based compounds. In 2016, Fe, Mn, and Ni were used to replace V to synthesize a series of materials of $Na_4VM(PO_4)_3$ (M = Fe, Mn, Ni) [48]. Similar to LMFP, the operating potential of $Na_4VMn(PO_4)_3$ can be significantly improved without capacity fading. Immediately, researchers focused on enhancing the electrochemical performance of Na₄VMn(PO₄)₃ [54–60]. However, as shown in figure 2(c), the $V^{4+/5+}$ redox couple is irreversible in $Na_4VMn(PO_4)_3$. It should be noted that the multi-electron transfer reaction is one of the prerequisites for high capacity NASICON-type cathodes. Therefore, the failure mechanism and how to realize a reversible $V^{4+/5+}$ redox couple are crucial. In 2020, Liu *et al* [61] revealed that the small ion radius of V^{5+} can migrate to Na_vacancy sites and block the sodium ion pathway in Na₃VCr(PO₄)₃. Interestingly, a similar phenomenon was captured in $Na_3VSc(PO_4)_3$, and a slightly reversible capacity at the 4.0 V platform was shown at -20 °C [62]. Based on the above finding, we can speculate that the transition metal migration of V^{5+} is a common issue of the irreversible $V^{4+/5+}$ redox couple. It should be noted that the replacing elements of Al^{3+} , Cr^{3+} , and Ga^{3+} make the V^{4+/5+} redox couple reaction reversible, and a platform located at 4.0 V (vs. Na⁺/Na) occurred in the discharge curve (figure 2(d)) [63–66]. This finding can be attributed to the small Al³⁺ and the eliminated Jahn–Teller effect of Mn^{3+} , so the crystal structure can be stable. In addition, the modification of polyanion groups in the NASICON framework also can be considered [67]. However, the above conclusions are inferred based on the reported experimental results, and research on such topics is still limited [68]. Therefore, we must pay attention to such issues and draw a whole picture of failure mechanisms or optimization strategies.

Furthermore, benefitting from the stronger electronegativity of F^- , the partial substitution of V-F for V-O can significantly improve the operating voltage of V-based cathode materials [50]. In recent years, fluorine-containing vanadium-based polyanion compounds such as NaVPO₄F [69, 70], Na₃V₂(PO₄)₂F₃ [71–74], and Na₃V₂O_{2x}(PO₄)₂F_{3-2x} [28, 75–77] have been reported as cathodes for NIBs (figures 2(a) and (b)). Although the above cathodes deliver a reversible specific capacity of ~120 mAh g⁻¹, the crystal structure will collapse when the V valence exceeds +4. In 2019, Yan *et al* [78] showed a



Figure 2. (a) Crystal structures and (b) voltage profiles of the typical V-based NASICON-type cathode materials, data from [69, 70, 79, 80]. (c) Charge curves of the V^{3+} to V^{5+} in which the $V^{4+/5+}$ redox couple is irreversible, data from [54, 62]. (d) Voltage profiles of the reversible $V^{4+/5+}$ redox couple reactions, data from [46].

detailed picture of the structural evolution of $Na_3V_2(PO_4)_2F_3$ when more than 2.5 sodium ions were extracted. In addition, they revealed that the $Na_0V_2(PO_4)_2F_3$ phase accommodates sodium in a disordered way and does not convert back to the initial structure. The aforementioned experimental results indicate that more than 1Na/TM can be extracted upon further charging, but the structural collapse occurs simultaneously. Therefore, this is the key problem of V-based high-capacity cathodes.

3.2. Mn-based NASICON cathodes

Manganese-based electrode materials are attractive due to their excellent stability, resource non-criticality, and high electrode potential [24, 81]. Currently, Mn-rich NASICON-type phosphates provide high electrode potentials and robust anionic redox-free frameworks, such as Na₃MnTi(PO₄)₃ [25, 81–89], Na₃MnZr(PO₄)₃ [47, 90], and Na₄MnCr(PO₄)₃ [91-95] (figure 3(a)). In 2013, Pan *et al* [24] first proposed Na₃MnTi(PO₄)₃ and Na₃MnZr(PO₄)₃ as cathode materials for NIBs. Subsequently, Gao et al [25] successfully achieved a discharge capacity of 80 mAh g^{-1} in Na₃MnTi(PO₄)₃. It should be noted that the Mn^{2+/3+} and $Mn^{3+/4+}$ redox couples can be entirely activated within the voltage range of 2.5–4.2 V. The corresponding thermodynamic equilibrium potential is \sim 3.6 V and ~ 4.0 V, respectively. As shown in figure 3(b), the voltage profiles of Na₄MnAl(PO₄)₃, Na₃MnTi(PO₄)₃, and Na₃MnZr(PO₄)₃ exhibit initial capacity fading and voltage hysteresis ($Al^{3+} < Ti^{4+} < Zr^{4+}$). However, the significant capacity fading of Mn-rich NASICON-type cathodes arises in the initial cycle, and an outstanding cycling performance is displayed in the following cycles [86, 89]. This result means that the failure mechanism of Mn-based cathodes is different from that of V-based ones (V⁵⁺ migrates to Na_vacancy sites during charging). For the high-capacity cathode, Wang *et al* [93] found that Cr^{3+} can not only activate the $Mn^{2+/4+}$ redox couple, but $Cr^{3+/4+}$ is also electrochemically active in Na₄MnCr(PO₄)₃. Therefore, Na₄MnCr(PO₄)₃ exhibits a high reversible capacity of 150.3 mAh g^{-1} , which is close to the 1.5e^{-/}/TM transfer reaction, as shown in figure 3(c). Unfortunately, the high operating voltage and poor



Figure 3. (a) Crystal structures and (b) voltage profiles of the typical Mn-based NASICON-type cathode materials, data from [25, 47, 96]. (c) Charge/discharge curve of $Na_4MnCr(PO_4)_3$ within the range of 1.5–4.5 V.



Figure 4. (a) Crystal structures of the typical Fe-based NASICON-type cathode materials. (b) Abundance in Earth's crust [111] and (c) prices [112] of elements. (d) Potential vs. specific capacity plots for Na₄Fe₃(PO₄)₂(P₂O₇) [113], Na₂Fe₂(SO₄)₃ [108], Na₂FePO₄F [105], and Na₃Fe₂(PO₄)₃ [101] normalized to the theoretical specific capacity per one-electron Fe²⁺ \leftrightarrow Fe³⁺ transition from experimental data.

stability limit its application, and more study is needed to optimize the electrochemical performance.

3.3. Fe-based NASICON cathodes

Fe-based phosphate compounds play a dominant role in NIB cathode research, which is encouraged by the success of LiFePO₄ [97]. As shown in figures 4(b) and (c), the low cost and high resource abundance [23] of Fe/Na match the requirements of large-scale energy storage devices. However, the thermodynamically stable structure of NaFePO₄ is an electrochemically inactive maricite phase [98]. Furthermore, the electrode potential of the Fe^{2+/3+} reversible redox couple is ~2.4 V (vs. Na⁺/Na) in NASICON-type compounds [99–101]. The operating potential is too low for the cathode material. Subsequently, anion groups with stronger electronegativity are used to increase the thermodynamic equilibrium potential of the Na-Fe-P-O system (e.g. P₂O₇⁴⁻ [102–104], F⁻ [105, 106], etc). In 2012, Barpanda *et al* [104] found that Na₂FeP₂O₇ has a high theoretical specific capacity of 97 mAh g⁻¹, with the thermodynamic equilibrium potential of the Fe^{2+/3+} redox couple raised to ~3.0 V (vs. Na⁺/Na). However, the high molecular mass of P₂O₇⁴⁻ results in a limited capacity. Kim *et al* [26]

developed a new mixed-polyanion cathode for NIBs, $Na_4Fe_3(PO_4)_2(P_2O_7)$. $Na_4Fe_3(PO_4)_2(P_2O_7)$ [107–109] shows a robust open framework with 3D Na⁺ ion diffusion paths. It is a new striking Fe-based polyanion material due to its high theoretical capacity (~129 mAh g⁻¹), with an average discharge potential of ~3.1 V (vs. Na⁺/Na). In addition, $Na_2Fe_2(SO_4)_3$ [27, 110], $Na_3Fe_2(PO_4)(P_2O_7)$ [98, 105, 106], and Na_2FePO_4F [98, 105, 106] have also been considered candidates for advanced commercial NIB cathode materials (figure 4(d)).

For the active electrochemical elements, 4d elements have also been reported, except for the above reported 3d transition metal element redox couples. In 2018, NaMo₂(PO₄)₃ was confirmed to achieve stable electrochemical cycling based on the Mo^{3+/4+} redox couple [114] with a theoretical specific capacity of 98.2 mAh g⁻¹ at an equilibrium potential of 2.45 V. In addition, the reversible reactions of redox couples such as Nb^{4+/5+} [115], Ti^{3+/4+} [116], Zr^{3+/4+} [117], and Cr^{3+/4+} [93] have also been reported in NASICON-type materials. However, the thermodynamic equilibrium potentials of the above compounds are either too low or too high to be used in cathode materials, whereas the relevant research is still in the initial stage.

4. Multi-electron transfer reaction

The low mass ratio of the transition metal means that a multi-electron transfer reaction is required to go beyond the electrochemical performance of $LiFePO_4$ (LFP). We will reveal the issue of reported compounds and show the basic rule for designing high-capacity cathode materials around Na content, transition metal sites, and polyanion frameworks.

4.1. Na content and structural stability

The number of alkali metal sites in the NASICON structure is typically 1–4. Recently, researchers found that a new phase with a Na content of 5 will occur when the discharge potential is between 0 and 1 V [118], and the polyanion skeleton structure is unchanged. However, previous results have shown that the discharge voltage platform of the above structures is close to 0 V, which cannot be used as cathode materials. Therefore, we speculate that the highest Na content is ~4 among NASICON-type cathode materials. Furthermore, Yan *et al* [78] confirmed that structural collapse occurs in Na₀V₂(PO₄)₂F₃ when charged to 4.8 V. Similar phenomena have also been reported in other systems. Theoretical calculations also show that the skeleton structure of NASICON-type compounds is difficult to maintain due to the high formation energy when the Na content is lower than 1. The above finding shows that it is necessary to design a structure with a Na content close to 4 to ensure enough Na⁺ ions for extraction.

Notably, Liu *et al* [61] suggested that V^{5+} with a small ionic radius can diffuse to the Na1 site and induce kinetic hysteresis. According to the above result, the reversibility of the $V^{4+/5+}$ redox couple can be realized when maintaining the occupancy of the Na1 site at high voltage. Recently, many works have focused on Na1 and Na2 sites for developing low-cost and high-energy-density V-based NASICON-type cathode materials [63, 119]. However, Na⁺ ion diffusion in NASICON frameworks is completed by the cooperation of the Na1 and Na2 sites, which means the Na⁺ in the Na1 and Na2 sites are dynamically evolving throughout the charging and discharging process. Therefore, some V-based NASICON compounds with a Na content of 4 (e.g. Na₄VNi(PO₄)₃, etc) showed limited reversibility even if there was enough Na⁺ at the Na2 site in the pristine structure. Here, we pinpoint that rather than focusing on precisely controlling the Na⁺ content of Na1 and Na2 sites in the initial structure, it might be more necessary to ensure that Na1 is a thermodynamically/kinetically stable site in the



Figure 5. A voltage map of NASICON electrodes, $Na_x MM'(PO_4)_3$, where *M* and M' = Ti, V, Cr, Mn, Fe, Co, and Ni. The text in each box represents the redox couple and the corresponding voltage vs. Na^+/Na [120]. The redox couples and the corresponding electrode potentials are shown in boxes (e.g. the redox couple in the range of $3 \le x \le 4$ (x of $Na_x V_2(PO_4)_3$) is $V^{2+/3+}$, and the electrode potential is 1.5 V). Reproduced from [120] with permission from the Royal Society of Chemistry.

entire voltage platform of the $V^{4+/5+}$ redox couple. Meanwhile, blocking the migration channel of V^{5+} to the Na site is crucial too.

4.2. Selection of transition metal elements

The elements that can be placed in transition metal sites are shown in figure 5. To facilitate element screening, we propose the following notes. First, the total valence state of the transition metal site is +5, and the Na content can be 4, so multi-element co-union is needed (M and M' are +2 and +3, respectively). Second, previous studies have shown that V⁵⁺ easily migrates to the alkali sites, which may be the predominant issue for the irreversibility of V^{4+/5+} redox couples (e.g. Na₄VMn(PO₄)₃, Na₄VFe(PO₄)₃, Na₄VNi(PO₄)₃, Na₃VSc(PO₄)₃, etc). Interestingly, the substitution of Al³⁺ and Ga³⁺ in group 13 (IIIA) can realize the reversible reaction of the V^{4+/5+} redox couple [41, 63]. Therefore, it is essential to understand the relationship between the reversibility of the V^{4+/5+} redox couple and the NASICON backbone. Finally, Mn^{2+/4+} is a significant step in developing low-cost NASICON-type cathode materials. However, the activation of Mn^{2+/4+} redox couples often relies on Al³⁺, Ti⁴⁺, and Zr⁴⁺, which cannot be used for high energy density materials (the +4 valence state of Ti and

Zr is too high, and Al³⁺ is electrochemically inactive) [24]. Excitingly, recent results have shown that Cr^{3+} can also activate the $Mn^{2+/4+}$ redox couple, and the $Cr^{3+/4+}$ redox reaction can be conducted at ~4.4 V platform [93], suggesting a promising material that deep research is necessary to improve its electrochemical performance. Likewise, exploring other electrochemically active +3-valent elements for activating $Mn^{2+/4+}$ is also a feasible strategy.

4.3. Polyanion frameworks

The polyanion groups are various, such as BO_3^{3-} , CO_3^{2-} , $C_2O_4^{2-}$, SiO_4^{4-} , PO_4^{3-} , SO_4^{2-} , etc. Currently, the reported materials with excellent electrochemical performance are mainly phosphate-based compounds, and the exploration of other anionic groups is still limited. In addition, researchers demonstrated that F, Cl, etc, were able to replace the O sites, which endowed an abundant selection of polyanion frameworks. Therefore, except for focusing on the element replacement of Na_xMM'(PO₄)₃, more polyanion frameworks also need to be explored.

5. Future perspectives

The low cost, wide distribution, and abundant reserves of sodium resources triggered the research of Na-ion batteries (NIBs) in the energy storage devices field. More notably, polyanionic-type NIB cathode materials are expected to meet the expansive demands for large-scale applications, benefitting from their long-term stability and high safety. Since our group first proposed the Mn-rich cathodes, several low cost NASICON cathodes with excellent cycling performance have been reported. However, the low transition metal mass fraction (for example, Fe is 35.4 wt% in LiFePO₄, and V is 22.35 wt% in Na₃V₂(PO₄)₃) of the above compounds leads to a limited theoretical specific capacity. Additionally, the costs of the total batteries are much higher than the costs of the active materials as additional items, such as electrolytes, binders, casings, and even the electric battery management system, are included. Therefore, a higher capacity is needed for developing advanced polyanionic-type NIB cathode materials, which can further reduce the cost of inactive material. For the next generation of NASICON-type cathode materials, the low transition metal mass ratio means that the multi-electron transfer reaction is essential for high-capacity NASICON-type cathode materials.

Through extensive literature review, we demonstrate the key challenge of realizing the 1.5e⁻/TM transfer reaction and delivering design rules from Na content, transition metal sites, and polyanion frameworks. Fortunately, the flexible structure gives a promising future in designing multi-electron transfer reaction NASICON-type cathode materials. Although it is important to develop new materials, it is equally essential to focus on the failure mechanism of reported high-capacity systems (such as Na₄VMn(PO₄)₃, Na₄VFe(PO₄)₃, Na₄MnCr(PO₄)₃, etc.). Overall, the characteristics of polyanionic compounds differ substantially from those of traditional layered oxide materials, and in-depth research is needed.

Acknowledgments

This work was supported by the National Key R&D Program of China (2022YFB3807800), National Natural Science Foundation (NSFC) of China (51725206, 52122214, 52002394, and 52072403), and Youth Innovation Promotion Association of the Chinese Academy of Sciences (2020006).

ORCID iDs

Yuan Liu b https://orcid.org/0000-0002-1366-3730 Xiaohui Rong b https://orcid.org/0000-0002-9786-4424

References

- Grosjean C, Miranda P H, Perrin M and Poggi P 2012 Assessment of world lithium resources and consequences of their geographic distribution on the expected development of the electric vehicle industry *Renew. Sustain. Energy Rev.* 16 1735–44
- [2] Kesler S E, Gruber P W, Medina P A, Keoleian G A, Everson M P and Wallington T J 2012 Global lithium resources: relative importance of pegmatite, brine and other deposits *Ore Geol. Rev.* 48 55–69
- [3] Miedema J H and Moll H C 2013 Lithium availability in the EU27 for battery-driven vehicles: the impact of recycling and substitution on the confrontation between supply and demand until 2050 *Resour. Policy* 38 204–11
- [4] Romero H, Méndez M and Smith P 2012 Mining development and environmental injustice in the Atacama desert of Northern Chile *Environ. Justice* 5 70–76
- [5] Slater M D, Kim D, Lee E and Johnson C S 2013 Sodium-ion batteries Adv. Funct. Mater. 23 947–58
- [6] Vaalma C, Buchholz D, Weil M and Passerini S 2018 A cost and resource analysis of sodium-ion batteries Nat. Rev. Mater. 3 1–11
- Zhao C *et al* 2020 Rational design of layered oxide materials for sodium-ion batteries Science 370 708–11
- [8] Zaghib K, Dubé J, Dallaire A, Galoustov K, Guerfi A, Ramanathan M, Benmayza A, Prakash J, Mauger A and Julien C M 2012 Enhanced thermal safety and high power performance of carbon-coated LiFePO₄ olivine cathode for Li-ion batteries *J. Power Sources* 219 36–44
- [9] Jin T, Li H, Zhu K, Wang P F, Liu P and Jiao L 2020 Polyanion-type cathode materials for sodium-ion batteries *Chem. Soc. Rev.* 49 2342–77
- [10] Rajagopalan R, Zhang Z, Tang Y, Jia C, Ji X and Wang H 2021 Understanding crystal structures, ion diffusion mechanisms and sodium storage behaviors of NASICON materials *Energy Storage Mater.* 34 171–93
- [11] Anantharamulu N, Koteswara Rao K, Rambabu G, Vijaya Kumar B, Radha V and Vithal M 2011 A wide-ranging review on NASICON-type materials J. Mater. Sci. 46 2821–37
- [12] Chen S, Wu C, Shen L, Zhu C, Huang Y, Xi K, Maier J and Yu Y 2017 Challenges and perspectives for NASICON-type electrode materials for advanced sodium-ion batteries *Adv. Mater. Weinheim* 29 1700431
- [13] Hagman L-O, Kierkegaard P, Karvonen P, Virtanen A I and Paasivirta J 1968 The crystal structure of NaM^{IV}₂(PO₄)₃; Me^{IV} = Ge, Ti, Zr Acta Chem. Scand. 22 1822–32
- [14] Goodenough J B 1976 Hong HYP and Kafalas JA Fast Na⁺-ion transport in skeleton structures *Mater. Res. Bull.* 11 203–20
- [15] Hong H Y P 1976 Crystal structures and crystal chemistry in the system Na_{1+x}Zr₂Si_xP_{3-x}O₁₂ Mater. Res. Bull. 11 173–82
- [16] Nadiri A, Delmas C, Salmon R and Hagenmuller P 1985 Chemical and electrochemical alkali metal intercalation in the iron(III) molybdate Fe₂(MoO₄)₃ Chem. Inf.-Dienst 16 537–44
- [17] Delmas C, Nadiri A and Soubeyroux J L 1988 The NASICON-type titanium phosphates ATi₂(PO₄)₃ (A=Li, Na) as electrode materials *Solid State Ion*. 28–30 419–23
- [18] Uebou Y, Kiyabu T, Okada S and Yamaki J-I 2002 Electrochemical sodium insertion into the 3D-framework of Na₃M₂(PO₄)₃(M=Fe, V) *Rep. Res. Inst. Appl. Mech. Kyushu Univ.* 16 1–5
- [19] Delmas C, Olazcuaga R, Cherkaoui F, Brochu R and Le Flem G 1978 A new family of phosphates with the formula Na₃M₂(PO₄)₃ (M = Ti, V, Cr, Fe) C. R. Acad. Sci. 10 168–74
- [20] Jian Z, Zhao L, Pan H, Hu Y-S, Li H, Chen W and Chen L 2012 Carbon coated Na₃V₂(PO₄)₃ as novel electrode material for sodium ion batteries *Electrochem. Commun.* 14 86–89
- [21] Liang L, Li X, Zhao F, Zhang J, Liu Y, Hou L and Yuan C 2021 Construction and operating mechanism of high-rate Mo-doped Na₃V₂(PO₄)₃@C nanowires toward practicable wide-temperature-tolerance Na-ion and hybrid Li/Na-ion batteries Adv. Energy Mater. 11 2100287
- [22] Xiong H, Sun G, Liu Z, Zhang L, Li L, Zhang W, Du F and Qiao Z A 2021 Polymer stabilized droplet templating towards tunable hierarchical porosity in single crystalline Na₃V₂(PO₄)₃ for enhanced sodium-ion storage *Angew. Chem., Int. Ed.* **60** 10334–41
- [23] Vesborg P C K and Jaramillo T F 2012 Addressing the terawatt challenge: scalability in the supply of chemical elements for renewable energy RSC Adv. 2 7933–47
- [24] Pan H, Hu Y-S and Chen L 2013 Room-temperature stationary sodium-ion batteries for large-scale electric energy storage *Energy Environ. Sci.* 6 2338–60

- [25] Gao H, Li Y, Park K and Goodenough J B 2016 Sodium extraction from NASICON-structured Na₃MnTi(PO₄)₃ through Mn(III)/Mn(II) and Mn(IV)/Mn(III) redox couples *Chem. Mater.* 28 6553–9
- [26] Kim H, Park I, Seo D-H, Lee S, Kim S-W, Kwon W J, Park Y-U, Kim C S, Jeon S and Kang K 2012 New iron-based mixed-polyanion cathodes for lithium and sodium rechargeable batteries: combined first principles calculations and experimental study J. Am. Chem. Soc. 134 10369–72
- [27] Cao Y, Yang C, Liu Y, Xia X, Zhao D, Cao Y, Yang H, Zhang J, Lu J and Xia Y 2020 A new polyanion Na₃Fe₂(PO₄)P₂O₇ cathode with high electrochemical performance for sodium-ion batteries ACS Energy Lett. 5 3788–96
- [28] Park Y U, Seo D-H, Kim B, Hong K-P, Kim H, Lee S, Shakoor R A, Miyasaka K, Tarascon J-M and Kang K 2012 Tailoring a fluorophosphate as a novel 4 V cathode for lithium-ion batteries *Sci. Rep.* 2 704
- [29] Jian Z et al 2014 Atomic structure and kinetics of NASICON Na_xV₂(PO₄)₃ cathode for sodium-ion batteries Adv. Funct. Mater. 24 4265–72
- [30] Zou Z et al 2021 Identifying migration channels and bottlenecks in monoclinic NASICON-type solid electrolytes with hierarchical ion-transport algorithms Adv. Funct. Mater. 31 2107747
- [31] Qiu Q, Li C, Liu H, Liao Y, Zhao C, Geng F, Shen M, Li J, Tong W and Hu B 2021 NMR evidence for the multielectron reaction mechanism of Na₃V₂(PO₄)₃ cathode and the impact of polyanion site substitution *J. Phys. Chem.* C 125 15200–9
- [32] Park S, Wang Z, Deng Z, Moog I, Canepa P, Fauth F, Carlier D, Croguennec L, Masquelier C and Chotard J-N 2021 Crystal structure of Na₂V₂(PO₄)₃, an intriguing phase spotted in the Na₃V₂(PO₄)₃–Na₁V₂(PO₄)₃ system *Chem. Mater.* 34 451–62
- [33] Li S, Dong Y, Xu L, Xu X, He L and Mai L 2014 Effect of carbon matrix dimensions on the electrochemical properties of Na₃V₂(PO₄)₃ nanograins for high-performance symmetric sodium-ion batteries Adv. Mater. Weinheim 26 3545–53
- [34] Zhu C, Song K, van Aken P A, Maier J and Yu Y 2014 Carbon-coated Na₃V₂(PO₄)₃ embedded in porous carbon matrix: an ultrafast Na-storage cathode with the potential of outperforming Li cathodes *Nano Lett.* 14 2175–80
- [35] Dou X, Hasa I, Saurel D, Vaalma C, Wu L, Buchholz D, Bresser D, Komaba S and Passerini S 2019 Hard carbons for sodium-ion batteries: structure, analysis, sustainability, and electrochemistry *Mater. Today* 23 87–104
- [36] Oh J A S, He H, Sun J, Cao X, Chua B, Huang Y, Zeng K and Lu L 2020 Dual-nitrogen-doped carbon decorated on Na₃V₂(PO₄)₃ to stabilize the intercalation of three sodium ions ACS Appl. Energy Mater. 3 6870–9
- [37] Yi G-D, Fan C-L, Hu Z, Zhang W-H, Han S-C and Liu J-S 2021 Construction of high performance N-doped Na₃V₂(PO₄)₂F₃/C cathode assisting by plasma enhanced chemical vapor deposition for sodium-ion batteries *Electrochim. Acta* 383 138370
- [38] An Q, Xiong F, Wei Q, Sheng J, He L, Ma D, Yao Y and Mai L 2015 Nanoflake-assembled hierarchical Na₃V₂(PO₄)₃/C microflowers: superior Li storage performance and insertion/extraction mechanism Adv. Energy Mater. 5 1401963
- [39] Yan J, Yuan W, Tang Z-Y, Xie H, Mao W-F and Ma L 2012 Synthesis and electrochemical performance of Li₃V₂(PO₄)_{3-x}Cl_x/C cathode materials for lithium-ion batteries *J. Power Sources* 209 251–6
- [40] Peng M, Zhang D, Zheng L, Wang X, Lin Y, Xia D, Sun Y and Guo G 2017 Hierarchical Ru-doped sodium vanadium fluorophosphates hollow microspheres as a cathode of enhanced superior rate capability and ultralong stability for sodium-ion batteries *Nano Energy* **31** 64–73
- [41] Hu Q, Liao J-Y, He X-D, Wang S, Xiao L-N, Ding X and Chen C-H 2019 *In situ* catalytic formation of graphene-like graphitic layer decoration on Na₃V_{2-x}Ga_x(PO₄)₃ (0 ≤ x ≤ 0.6) for ultrafast and high energy sodium storage *J. Mater. Chem.* A 7 4660–7
- [42] Bi L, Liu X, Li X, Chen B, Zheng Q, Xie F, Huo Y and Lin D 2020 Modulation of the crystal structure and ultralong life span of a Na₃V₂(PO₄)₃-based cathode for a high-performance sodium-ion battery by niobium-vanadium substitution *Ind. Eng. Chem. Res.* 59 21039–46
- [43] Park J Y et al 2020 An iron-doped NASICON type sodium ion battery cathode for enhanced sodium storage performance and its full cell applications J. Mater. Chem. A 8 20436–45
- [44] Chen Y, Cheng J, Sun S, Tian Z, Jiang X, Wang Y, He Z, Liu C, Huang Q and Guo L 2021 Constructing hierarchical porous Fe/F-codoped Na₃V₂(PO₄)₃/C composite enwrapped with carbon nanotubes as high-performance cathode for symmetric sodium ion batteries *J. Power Sources* **513** 230545
- [45] Ghosh S, Jose N, Senthilkumar B, Amonpattaratkit P and Senguttuvan P 2021 Multi-redox (V⁵⁺/V⁴⁺/V³⁺/V²⁺) driven asymmetric sodium (de)intercalation reactions in NASICON-Na₃VIn(PO₄)₃ cathode J. Electrochem. Soc. 168 050534
- [46] Liu R et al 2017 Exploring highly reversible 1.5-electron reactions (V³⁺/V⁴⁺/V⁵⁺) in Na₃VCr(PO₄)₃ cathode for sodium-ion batteries ACS Appl. Mater. Interfaces 9 43632–9
- [47] Gao H, Seymour I D, Xin S, Xue L, Henkelman G and Goodenough J B 2018 Na₃MnZr(PO₄)₃: a high-voltage cathode for sodium batteries *J. Am. Chem. Soc.* 140 18192–9

- [48] Zhou W, Xue L, Lü X, Gao H, Li Y, Xin S, Fu G, Cui Z, Zhu Y and Goodenough J B 2016 Na_xMV(PO₄)₃ (M = Mn, Fe, Ni) structure and properties for sodium extraction *Nano Lett.* 16 7836–41
- [49] Zhang X, Rui X, Chen D, Tan H, Yang D, Huang S and Yu Y 2019 Na₃V₂(PO₄)₃: an advanced cathode for sodium-ion batteries *Nanoscale* 11 2556–76
- [50] Boivin E, Chotard J N, Masquelier C and Croguennec L 2021 Towards reversible high-voltage multi-electron reactions in alkali-ion batteries using vanadium phosphate positive electrode materials *Molecules* 26 1428
- [51] Lv Z, Ling M, Yue M, Li X, Song M, Zheng Q and Zhang H 2021 Vanadium-based polyanionic compounds as cathode materials for sodium-ion batteries: toward high-energy and high-power applications *J. Energy Chem.* 55 361–90
- [52] Chotard J-N, Rousse G, David R, Mentré O, Courty M and Masquelier C 2015 Discovery of a sodium-ordered form of Na₃V₂(PO₄)₃ below ambient temperature *Chem. Mater.* 27 5982–7
- [53] Rui X, Sun W, Wu C, Yu Y and Yan Q 2015 An advanced sodium-ion battery composed of carbon coated Na₃V₂(PO₄)₃ in a porous graphene network *Adv. Mater. Weinheim* 27 6670–6
- [54] Chen F, Kovrugin V M, David R, Mentré O, Fauth F, Chotard J N and Masquelier C 2018 A NASICON-type positive electrode for Na batteries with high energy density: Na₄MnV(PO₄)₃ Small Methods 3 1800218
- [55] Ghosh S, Barman N, Mazumder M, Pati S K, Rousse G and Senguttuvan P 2019 High capacity and high-rate NASICON-Na_{3.75}V_{1.25}Mn_{0.75}(PO₄)₃ cathode for Na-ion batteries via modulating electronic and crystal structures *Adv. Energy Mater.* **10** 1902918
- [56] Anishchenko D V, Zakharkin M V, Nikitina V A, Stevenson K J and Antipov E V 2020 Phase boundary propagation kinetics predominately limit the rate capability of NASICON-type Na_{3+x}Mn_xV_{2-x}(PO₄)₃ (0≤x≤1) materials *Electrochim. Acta* 354 136761
- [57] Ghosh S, Barman N and Senguttuvan P 2020 Impact of Mg²⁺ and Al³⁺ substitutions on the structural and electrochemical properties of NASICON-Na_xVMn_{0.75}M_{0.25}(PO₄)₃ (M= Mg and Al) cathodes for sodium-ion batteries *Small* 16 e2003973
- [58] Ma X, Cao X, Zhou Y, Guo S, Shi X, Fang G, Pan A, Lu B, Zhou J and Liang S 2020 Tuning crystal structure and redox potential of NASICON-type cathodes for sodium-ion batteries *Nano Res.* 13 3330–7
- [59] Xu C et al 2021 A novel NASICON-typed Na₄VMn_{0.5}Fe_{0.5}(PO₄)₃ cathode for high-performance Na-ion batteries Adv. Energy Mater. 11 2100729
- [60] Zhang J, Zhao X, Song Y, Li Q, Liu Y, Chen J and Xing X 2019 Understanding the superior sodium-ion storage in a novel Na_{3.5}Mn_{0.5}V_{1.5}(PO₄)₃ cathode *Energy Stor. Mater.* 23 25–34
- [61] Liu R, Zheng S, Yuan Y, Yu P, Liang Z, Zhao W, Shahbazian-Yassar R, Ding J, Lu J and Yang Y 2020 Counter-intuitive structural instability aroused by transition metal migration in polyanionic sodium ion host Adv. Energy Mater. 11 2003256
- [62] Perfilyeva T I et al 2021 Complete three-electron vanadium redox in NASICON-type Na₃VSc(PO₄)₃ electrode material for Na-ion batteries J. Electrochem. Soc. 168 110550
- [63] Wang Q, Gao H, Li J, Liu G B and Jin H 2021 Importance of crystallographic sites on sodium-ion extraction from NASICON-structured cathodes for sodium-ion batteries ACS Appl. Mater. Interfaces 13 14312–20
- [64] Sun C, Zhao Y, Ni Q, Sun Z, Yuan X, Li J and Jin H 2022 Reversible multielectron redox in NASICON cathode with high energy density for low-temperature sodium-ion batteries *Energy Stor. Mater.* 49 291–8
- [65] Li M, Sun C, Ni Q, Sun Z, Liu Y, Li Y, Li L, Jin H and Zhao Y 2023 High entropy enabling the reversible redox reaction of V⁴⁺/V⁵⁺ couple in NASICON-type sodium ion cathode *Adv. Energy Mater.* 13 2203971
- [66] Zhao Y, Gao X, Gao H, Jin H and Goodenough J B 2020 Three electron reversible redox reaction in sodium vanadium chromium phosphate as a high-energy-density cathode for sodium-ion batteries Adv. Funct. Mater. 30 1908680
- [67] Liu Y, Sun C, Ni Q, Sun Z, Li M, Ma S, Jin H and Zhao Y 2022 Enhanced electrochemical performance of NASICON-type sodium ion cathode based on charge balance theory *Energy Stor Mater*. 53 881–9
- [68] Liu Y, Li J, Shen Q, Zhang J, He P, Qu X and Liu Y 2022 Advanced characterizations and measurements for sodium-ion batteries with NASICON-type cathode materials *eScience* 2 10–31
- [69] Ling M, Lv Z, Li F, Zhao J, Zhang H, Hou G, Zheng Q and Li X 2020 Revisiting of tetragonal NaVPO₄F: a high energy density cathode for sodium-ion batteries ACS Appl. Mater. Interfaces 12 30510–9
- [70] Shraer S D et al 2022 Development of vanadium-based polyanion positive electrode active materials for high-voltage sodium-based batteries Nat. Commun. 13 4097
- [71] Le Meins J M, Crosnier-Lopez M P, Hemon-Ribaud A and Courbion G 1999 Phase transitions in the Na₃M₂(PO₄)₂F₃ family (M=Al³⁺, V³⁺, Cr³⁺, Fe³⁺, Ga³⁺): synthesis, thermal, structural, and magnetic studies *J. Solid State Chem.* **148** 260–77

- [72] Gover R, Bryan A, Burns P and Barker J 2006 The electrochemical insertion properties of sodium vanadium fluorophosphate, Na₃V₂(PO₄)₂F₃ Solid State Ion. 177 1495–500
- [73] Xu M, Xiao P, Stauffer S, Song J, Henkelman G and Goodenough J B 2014 Theoretical and experimental study of vanadium-based fluorophosphate cathodes for rechargeable batteries *Chem. Mater.* 26 3089–97
- [74] Dacek S T, Richards W D, Kitchaev D A and Ceder G 2016 Structure and dynamics of fluorophosphate Na-ion battery cathodes *Chem. Mater.* 28 5450–60
- [75] Massa W, Yakubovich O V and Dimitrova O V 2002 Crystal structure of a new sodium vanadyl(IV) fluoride phosphate Na₃{V₂O₂F[PO₄]₂} Solid State Sci. 4 495–501
- [76] Park Y U, Seo D H, Kwon H S, Kim B, Kim J, Kim H, Kim I, Yoo H I and Kang K 2013 A new high-energy cathode for a Na-ion battery with ultrahigh stability J. Am. Chem. Soc. 135 13870–8
- [77] Kumar P R, Jung Y H, Lim C H and Kim D K 2015 Na₃V₂O_{2x}(PO₄)₂F_{3-2x}: a stable and high-voltage cathode material for aqueous sodium-ion batteries with high energy density *J. Mater. Chem.* A 3 6271–5
- [78] Yan G, Mariyappan S, Rousse G, Jacquet Q, Deschamps M, David R, Mirvaux B, Freeland J W and Tarascon J M 2019 Higher energy and safer sodium ion batteries via an electrochemically made disordered Na₃V₂(PO₄)₂F₃ material *Nat. Commun.* 10 585
- [79] Bianchini M, Fauth F, Brisset N, Weill F, Suard E, Masquelier C and Croguennec L 2015 Comprehensive investigation of the Na₃V₂(PO₄)₂F₃-NaV₂(PO₄)₂F₃ system by operando high resolution synchrotron x-ray diffraction *Chem. Mater.* 27 3009–20
- [80] Guo J Z, Wang P F, Wu X L, Zhang X H, Yan Q, Chen H, Zhang J P and Guo Y G 2017 High-energy/power and low-temperature cathode for sodium-ion batteries: *in situ* XRD study and superior full-cell performance *Adv. Mater. Weinheim* 29 1701968
- [81] Snarskis G, Pilipavicius J, Gryaznov D, Mikoliu Naite L and Vilciauskas L 2021 Peculiarities of phase formation in Mn-based Na superIonic conductor (NaSICon) systems: the case of Na_{1+2x}Mn_xTi_{2-x}(PO₄)₃ (0.0≤ x≤ 1 5 Chem. Mater. 33 8394–403
- [82] Zhou Y, Shao X, Lam K H, Zheng Y, Zhao L, Wang K, Zhao J, Chen F and Hou X 2020 Symmetric sodium-ion battery based on dual-electron reactions of NASICON-structured Na₃MnTi(PO₄)₃ material ACS Appl. Mater. Interfaces 12 30328–35
- [83] Liu J, Lin K, Zhao Y, Zhou Y, Hou X, Liu X, Lou H, Lam K-H and Chen F 2021 Exceeding three-electron reactions in Na_{3+2x}Mn_{1+x}Ti_{1-x}(PO₄)₃ NASICON cathodes with high energy density for sodium-ion batteries J. Mater. Chem. A 9 10437–46
- [84] Li H, Xu M, Gao C, Zhang W, Zhang Z, Lai Y and Jiao L 2020 Highly efficient, fast and reversible multi-electron reaction of Na₃MnTi(PO₄)₃ cathode for sodium-ion batteries *Energy Storage Mater.* 26 325–33
- [85] Zhu T et al 2019 Realizing three-electron redox reactions in NASICON-structured Na₃MnTi(PO₄)₃ for sodium-ion batteries Adv. Energy Mater. 9 2338–60
- [86] Zhu T, Hu P, Cai C, Liu Z, Hu G, Kuang Q, Mai L and Zhou L 2020 Dual carbon decorated Na₃MnTi(PO₄)₃: a high-energy-density cathode material for sodium-ion batteries *Nano Energy* 70 104548
- [87] Sun X, Wang T, Zhang W, Li H, Lai Y and Zhang Z 2020 Dual carbon decorated Na₃MnTi(PO₄)₃ as an advanced cathode for sodium-ion batteries *Ionics* 26 3919–27
- [88] Gao H and Goodenough J B 2016 An aqueous symmetric sodium-ion battery with NASICON-structured Na₃MnTi(PO₄)₃ Angew. Chem., Int. Ed. 55 12768–72
- [89] Zhang J, Lin C, Xia Q, Wang C and Zhao X S 2021 Improved performance of Na₃MnTi(PO₄)₃ using a non-stoichiometric synthesis strategy ACS Energy Lett. 6 2081–9
- [90] Ma X, Wu X, Liu Y, Wu W, Pan Z and Shen P K 2021 Toward a high-energy-density cathode with enhanced temperature adaptability for sodium-ion batteries: a case study of Na₃MnZr(PO₄)₃ microspheres with embedded dual-carbon networks ACS Appl. Mater. Interfaces 13 21390–400
- [91] Zhang J, Liu Y, Zhao X, He L, Liu H, Song Y, Sun S, Li Q, Xing X and Chen J 2020 A novel NASICON-type Na₄MnCr(PO₄)₃ demonstrating the energy density record of phosphate cathodes for sodium-ion batteries *Adv. Mater. Weinheim* **32** 1906348
- [92] Zhang W, Li H, Zhang Z, Xu M, Lai Y and Chou S L 2020 Full activation of Mn⁴⁺/Mn³⁺ redox in Na₄MnCr(PO₄)₃ as a high-voltage and high-rate cathode material for sodium-ion batteries *Small* 16 e2001524
- [93] Wang J, Wang Y, Seo D H, Shi T, Chen S, Tian Y, Kim H and Ceder G 2020 A high-energy NASICON-type cathode material for Na-ion batteries Adv. Energy Mater. 10 1903968
- [94] Zhao Y, Gao X, Gao H, Dolocan A and Goodenough J B 2021 Elevating energy density for sodium-ion batteries through multielectron reactions *Nano Lett.* 21 2281–7
- [95] Li J et al 2022 Stabilized multi-electron reactions in a high-energy Na₄Mn_{0.9}CrMg_{0.1}(PO₄)₃ sodium-storage cathode enabled by the pinning effect Small 18 e2202879
- [96] Wang Q, Ling C, Li J, Gao H, Wang Z and Jin H 2021 Experimental and theoretical investigation of Na₄MnAl(PO₄)₃ cathode material for sodium-ion batteries *Chem. Eng. J.* 425 130680
- [97] He L, Li H, Ge X, Li S, Wang X, Wang S, Zhang L and Zhang Z 2022 Iron-phosphate-based cathode materials for cost-effective sodium-ion batteries: development, challenges, and prospects Adv. Mater. Interfaces 9 2200515

- [98] Avdeev M, Mohamed Z, Ling C D, Lu J, Tamaru M, Yamada A and Barpanda P 2013 Magnetic structures of NaFePO₄ maricite and triphylite polymorphs for sodium-ion batteries *Inorg. Chem.* 52 8685–93
- [99] Cao Y J, Liu Y, Zhao D Q, Xia X P, Zhang L C, Zhang J X, Yang H S and Xia Y Y 2020 Highly stable Na₃Fe₂(PO₄)₃@hard carbon sodium-ion full cell for low-cost energy storage ACS Sustain. Chem. Eng. 8 1380–7
- [100] Qiu S et al 2019 NASICON-type Na₃Fe₂(PO₄)₃ as a low-cost and high-rate anode material for aqueous sodium-ion batteries Na₃Fe₂(PO₄)₃ as a low-cost and high-rate anode material for aqueous sodium-ion batteries Nano Energy 64 103941
- [101] Rajagopalan R et al 2017 Improved reversibility of Fe³⁺/Fe⁴⁺ redox couple in sodium super ion conductor type Na₃Fe₂(PO₄)₃ for sodium-ion batteries Adv. Mater. Weinheim 29 1605694
- [102] Barpanda P, Liu G D, Ling C D, Tamaru M, Avdeev M, Chung S C, Yamada Y and Yamada A 2013 Na₂FeP₂O₇: a safe cathode for rechargeable sodium-ion batteries *Chem. Mater.* 25 3480–7
- [103] Jung Y H, Lim C H, Kim J H and Kim D K 2014 Na₂FeP₂O₇ as a positive electrode material for rechargeable aqueous sodium-ion batteries *RSC Adv.* 4 9799–802
- [104] Barpanda P, Ye T, Nishimura S-I, Chung S-C, Yamada Y, Okubo M, Zhou H and Yamada A 2012 Sodium iron pyrophosphate: a novel 3.0 V iron-based cathode for sodium-ion batteries *Electrochem. Commun.* 24 116–9
- [105] Li H, Wang T, Wang S, Wang X, Xie Y, Hu J, Lai Y and Zhang Z 2021 Scalable synthesis of the Na₂FePO₄F cathode through an economical and reliable approach for sodium-ion batteries ACS Sustain. Chem. Eng. 9 11798–806
- [106] Dong J et al 2022 Electronic structure regulation of Na₂FePO₄F cathode toward superior high-rate and high-temperature sodium-ion batteries Energy Stor. Mater. 45 851–60
- [107] Barpanda P, Oyama G, Nishimura S, Chung S C and Yamada A 2014 A 3.8-V earth-abundant sodium battery electrode *Nat. Commun.* **5** 4358
- [108] Chen M et al 2018 A novel graphene oxide wrapped Na₂Fe₂(SO₄)₃/C cathode composite for long life and high energy density sodium-ion batteries Adv. Energy Mater. 8 1800944
- [109] Plewa A, Kulka A, Hanc E, Zając W, Sun J, Lu L and Molenda J 2020 Facile aqueous synthesis of high performance Na₂FeM(SO₄)₃ (M = Fe, Mn, Ni) alluaudites for low cost Na-ion batteries J. Mater. Chem. A 8 2728–40
- [110] Wang H, Pan Z, Zhang H, Dong C, Ding Y, Cao Y and Chen Z 2021 A green and scalable synthesis of Na₃Fe₂(PO₄)P₂O₇/rGO cathode for high-rate and long-life sodium-ion batteries *Small Methods* 5 e2100372
- [111] William M H, David R L and Thomas J B 2016 CRC Handbook of Chemistry and Physics; Abundance of Elements in the Earth's Crust and in the Sea 97th edn (Boca Raton, FL: CRC Press) pp 14–17
- [112] Trading economics 2022 (available at: https://tradingeconomics.com/)
- [113] Chen M *et al* 2019 NASICON-type air-stable and all-climate cathode for sodium-ion batteries with low cost and high-power density *Nat. Commun.* **10** 1480
- [114] Panin R V, Drozhzhin O A, Fedotov S S, Khasanova N R and Antipov E V 2018 NASICON-type NaMo₂(PO₄)₃: electrochemical activity of the Mo⁺⁴ polyanion compound in Na-cell *Electrochim. Acta* 289 168–74
- [115] Tillement O, Couturier J C, Angenault J and Quarton M 1991 Crystal chemistry and electrical study of Na_xNbTi(PO₄)₃ Solid State Ion. 48 249–55
- [116] Tillement O, Angenault J, Couturier J C and Quarton M 1992 Electrochemical studies of mixed valence NASICON Solid State Ion. 53-56 391–9
- [117] Wang W, Jiang B, Hu L and Jiao S 2014 NASICON material NaZr₂(PO₄)₃: a novel storage material for sodium-ion batteries J. Mater. Chem. A 2 1341–5
- [118] Jian Z, Sun Y and Ji X 2015 A new low-voltage plateau of Na₃V₂(PO₄)₃ as an anode for Na-ion batteries *Chem. Commun.* 51 6381–3
 [119] Xu C *et al* 2022 Reversible activation of V⁴⁺/V⁵⁺ redox couples in NASICON phosphate
- [119] Xu C et al 2022 Reversible activation of V⁴⁺/V³⁺ redox couples in NASICON phosphate cathodes Adv. Energy Mater. 12 2200966
- [120] Singh B, Wang Z, Park S, Gautam G S, Chotard J-N, Croguennec L, Carlier D, Cheetham A K, Masquelier C and Canepa P 2021 A chemical map of NASICON electrode materials for sodium-ion batteries J. Mater. Chem. A 9 281–92