Chapter 1

NASICON Electrodes for Sodium-Ion Batteries

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Abstract

The incessantly growing demand for energy storage is attracting the researcher’s attention to develop consistent, effective, and ecologically harmless electrochemical systems for energy storage. Sodium-ion batteries (SIBs) are emergent as one of the utmost efficient large-scale systems for energy storage due to the great accessibility of raw sodium resources and their cost-effective assets. Sodium Super Ionic Conductor (NASICON) electrodes-based materials have offered an opportunity precisely for SIBs as a next-generation energy storage device because of their unique properties. NASICON electrodes have been extensively proven to demonstrate enhanced and miscellaneous features for SIBs in terms of high rate competence, flexible battery structures, long cycling life, and high specific capacity, due to their outstanding characteristics such as high charge carrier mobility, excellent mechanical strength, high theoretical ability, high electronic conductivity, and large surface area. This chapter summarizes the important advancement accomplished on NASICON-based electrodes for application in SIBs, including both cathodes and anodes over the past decade. Furthermore, this chapter also focuses on the new challenges and commercial demand for SIBs and some perspectives on the use of NASICON-based electrodes for future SIB applications.

Keywords

NASICON, Electrodes, Energy Storage, SIBs, Cathodes, Anodes

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1. Introduction

In the fields of information, actuation, and energy conversion, lithium-ion batteries (LIBs) have been initiating extensively spread significance in the last two decades. They demonstrated enormous valuable for various needs, for example, robots, electric vehicles, and portable smart devices because of benefits in terms of volume density (250–650 Wh L⁻¹) and energy capacity (100–300 Wh kg⁻¹) [1-3]. Nowadays, due to the low abundance of lithium, LIBs face severe bottle-necks at a relatively high cost and limited energy densities. Thus, they are entering in the meadows of significant energy storage devices, especially for grid storage [4-6]. Sodium-ion batteries (SIBs) offer numerous applications compared to LIBs, for instance, consistently topographical dispersal, markedly low cost and plenty of elemental sources, henceforth recognized as a grave alternate to LIBs [7-9]. The demand for SIBs in terms of kinetic as well as thermodynamic criteria is certainly predictable to designate competitive with LIB systems [10]. Sometimes, the electrochemical performance of Na-ion batteries is superior to LIBs [11].
On a foremost peek, in comparison to Li, solemn drawbacks predicted due to the different location in the periodic table of the Na. The Na\(^+\) ions desertion and insertion hooked on a large number of host materials are not as good as intended for their Li-analogues, i.e., V\(_2\)O\(_5\), NaFePO\(_4\), Na\(_7\)V\(_3\)(P\(_2\)O\(_7\))\(_4\) and sodium oxides (NaMO\(_2\), M = Cu, V, Fe, Ni, Co, and Mn) [12-19]. However, despite these drawbacks, the “extrinsic” benefits of SIBs create them efficient for the use of energy storage devices. At another peek, the seeming “intrinsic” drawbacks must be appraised further: Polarizability of the sodium ion as well as the electro-positivity is higher. As a significance, the Li is used for most systems although the cell potential is not unavoidably higher of their respective Li-analogues. More prominently, the two key advantages of increased ionic radius are: (1) the transference resistance produced through transporting the ions into the electrode from the liquid electrolyte intended for exceedingly polarizing small Li-ion, is characteristically lesser due to the less severe solvation in liquid electrolytes. More prominently, the higher ionic radius is not attainable with Li, which allows solid structures with massive ion conductivities. β-alumina’s is a characteristic example which demonstrates that the sodium ion is of flawless polarizability and size. Likewise, sodium ion surpasses Li-ion conductivities having very high conductivities and in the Na-super ionic electrode in the NASICON family. Previously, various metal oxide materials have been synthesized by using chemical precipitation, hydrothermal, and sol-gel method which has been used for the detoxification of water [20-28], but these nanomaterials were not utilized for the conduction of electricity. Hence, some other metal oxides have been synthesized and applied, such as NASICON based materials which were used as conductor materials. As the tools of nanotechnology, because of the limited electronic conductivity, the electrode materials based on NASICON display inadequate chemical diffusion and must be practical to advance performance despite the so-induced varied conductivity [29-31]. The five main categories for present SIBs anodes are: (1) nonmetallic elements (S and P); [32,33] (2) metal oxides/selenides/phosphides/sulphides (SnS\(_2\), CoSe\(_2\), Sb\(_2\)S\(_3\), WS\(_2\), Sb\(_2\)O\(_4\), MoS\(_2\), TiO\(_2\), SnO\(_2\), NiP\(_3\), and CoSe); [34-43] (3) NASICON based materials (NaTi\(_2\)(PO\(_4\))\(_3\)); [44,45] (4) carbon-based materials (nitrogen-doped carbon nanofibers, porous, hard carbon); [46,47] and last but not least (5) alloys and metals (Ge, Sb, Sn-Ge, Na, Sn, and Sn-Ge-Sb); [48-53].

2. Machinery of SIBs

Characteristic SIBs are composed of four components which utilize as LIBs based on the rocking chair principle, [54] and i.e., non-aqueous salt containing electrolyte, a negative electrode, a positive electrode, and separator. Comprising NaClO\(_4\) (1M) ethylene carbonate/propylene carbonate as electrolyte used for the formation of the typical SIB.
The external circuit passes the electrons flow from the positive electrode towards the negative electrode throughout the charging process, and the Na\(^+\) ions leave characteristic cathode for example layered NaCoO\(_2\) or Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) and are fused in the anode while the process is reversed throughout discharging. For the reduction of the overall battery cost up to $70 per 100 m, battery grade, the aluminum foil can be utilized commercially for cathode and anode as a current collector [55]. In this chapter, we emphasize on NASICON electrode materials having physical steadiness and high ionic conductivity as the major advantages have previously been stated. The list ought to be completed by thermal stability and chemical flexibility. Providing pronounced Na\(^+\) diffusion channels, the NASICON framework construction is built by polyhedral XO\(_4\) groups and corner-shared MO\(_6\) (M'O\(_6\)) [56]. The cathodes materials in SIBs are made of various materials such as Na\(_3\)V\(_2\)(PO\(_4\))\(_2\)F\(_3\), Na\(_2\)FeTi(PO\(_4\))\(_3\), Na\(_{1.5}\)VPO\(_4\)F\(_{0.5}\), Fe\(_2\)(MoO\(_4\))\(_3\), and Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) [57-59]. Besides these materials, some other NASICON materials, for example, sodium salt of zirconium phosphate (NaZr\(_2\)(PO\(_4\))\(_3\)), Manganese-titanium mixed salts (Na\(_3\)MnTi(PO\(_4\))\(_3\)), sodium salt of titanium phosphate (NaTi\(_2\)(PO\(_4\))\(_3\)), and sodium salt of vanadium phosphate (NaV\(_2\)(PO\(_4\))\(_3\)) having low redox potential is pondered by means of anode material for SIBs and can be used as Ti\(^{3+}/Ti^{4+}\) conversion based NaTi\(_2\)(PO\(_4\))\(_3\) materials displays a reversible capacity of 120 mAh g\(^{-1}\) and a discharge voltage at 2.1 V [44]. The redox conversion of V\(^{3+}/V^{4+}\) in Na\(_3\)V\(_2\)(PO\(_4\))\(_3\) cathode material with high capacity (117 mAh g\(^{-1}\)) demonstrates a discharge current of 3.4 V, whereas the V\(^{2+}/V^{3+}\) redox conversion, chief as an anode material having a capacity (50 mAh g\(^{-1}\)) offers a lower energy of 1.6 V [60,61].

2.1 Storing the progression of NASICON materials

Primarily in the 1980s and 1990s, the ionic conductivity for NASICON solid electrolytes has been structurally analyzed and methodically measured. Goodenough, Kefalas, and Hong [62,63] worked on the material science of NASICON materials. Kreuer et al. [64] provided a complete description upon mechanisms of ion conductivity as well as kinetic stability, thermodynamic stability, and phase thermodynamics regarding sodium of the solid electrolyte. The absence of phosphate required for the thermodynamic stability against Na, which previously principals to a considerable subordinate conductivity [65]. If passivation layers are fashioned and lower temperature is pondered, this demonstrates the use of NASICON’s as solid electrolyte. However, in the NASICON electrode for the ion transport formulated the origin, the ion transport subjects elucidated in the electrolyte literature also [66,67]. The conversation of storage kinetics is not exclusively transported controlled and non-trivial. This is because of the super-position of diffusion and migration and the heterogeneity of the situation as well. The storing progression is a chemical diffusion problem when given sufficiently fast access of electrons (current
collecting phase) and ions (liquid electrolyte) to the electroactive particles, wherever
Equation 1 demonstrates the chemical diffusion coefficient [68]

\[
D_\delta \propto \tau_{\text{ion}} \frac{\sigma_{\text{ion}} + \sigma_{\text{eon}}}{\epsilon_{\text{eon}} + \epsilon_{\text{ion}}}
\]  

(1)

The concentration of the ionic and electronic transporters given as \( C_{\text{ion}} \) and \( C_{\text{eon}} \). The \( \chi \)-factors are typically critical at the process temperature and define internal trapping reactions. If we assume \( \sigma_{\text{ion}} \gg \sigma_{\text{eon}} \) and \( C_{\text{ion}} \gg C_{\text{eon}} \) for our NASICON materials.

\[
D_\delta \propto \chi_{\text{eon}} D_{\text{eon}}
\]  

(2)

The \( D_\delta \) is strong-minded through the trapping reactions (\( \chi \) factors) and electronic mobility (proportional to \( D_{\text{eon}} \)). The conduction of ions and electrons to the particles is next to the share of the transport kinetics. The conductivity of ions of NASICON materials assistance in ion filtration due to the permeable liquid electrolytes and morphologies, which is basically the transport of electrons that is essential.

Table 1 summarizes the distinctive chemical dispersal constants values of NASICON materials. Here, following abbreviation are utilized i.e. propylene carbonate (PC), dimethylsulfoxide (DMSO); fluoroethylene carbonate (FEC); bisphenol A ethoxylate dimethacrylate (BEMA); ethylene carbonate (EC); poly(ethylene glycol) methyl ether methacrylate (PEGMA); Room temperature (RT); Effective diffusion coefficient (EDC); diethyl carbonate (DEC); dimethyl carbonate (DMC).

Regrettably, literature values are essential effective values and affected by phase transformations, interfaces, or issues of size are frequently not measured bulk values consistently. The \( D_\delta \) values have been dependable at 150 °C to 1.6X10\(^{-9}\) cm\(^2\) S\(^{-1}\) on single crystalline LiFePO\(_4\) [86]. Finally, it was concluded that NASICON based materials offer above standards of most other electrode phases around 10\(^{-10}\) cm\(^2\) S\(^{-1}\). The NASICON materials are poor towards electric conductivity because of electronic wiring by the accumulation of current collecting phases, for example, by deliberate carbon coating, which is the example of carbon and additional conductive coating. In the electroactive particles, the transport kinetics is apprehension because of the relaxation time occurred due to two adjusting screws, the typical solutions are shown in Figure 1a, b [68].

\[
\tau_\delta \propto L^2/D_\delta
\]  

(3)
Where D is the chemical diffusion coefficient, τ is a biochemical dispersion duration, and L is the length of dispersion. The Dδ cannot be significantly stimulated.

Doping utmost assistances through increasing its influence on χ factor and \( D_{eon} \) by the increase in \( \sigma_{ion} \) or \( \sigma_{eon} \), in disrupting, the particles transference is shown in Equation (2) [87]. The particle size is the utmost operative parameter which arrives quadratically. Therefore, Figure 1c shows that nano-structuring is a delicate tool. For a one μm particle size a value leads to a minute storage time at \( 10^{-10} \) cm\(^2\) S\(^{-1}\).

### Table 1. The distinctive values of chemical diffusion coefficients.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Test environment</th>
<th>EDC (cm(^2) S(^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>FePO(_4); LiFePO(_4)</td>
<td>LiPF(_6) (1 M) at 20 °C in DMC/EC</td>
<td>1.8 X 10(^{-14}); 2.2 X 10(^{-16})</td>
<td>[69]</td>
</tr>
<tr>
<td>( Li_3V_2(PO_4)_3 )</td>
<td>LiPF(_6) (1 M) at 20 °C in DMC/EC (1:1, w/w)</td>
<td>( \approx 10^{-11} - 10^{-9} )</td>
<td>[70]</td>
</tr>
<tr>
<td>( P_2)-Na(<em>{2/3}[Ni(</em>{1/3})Mn(_{2/3})]O_2 )</td>
<td>LiPF(_6) in DEC/EC; NaPF(_6) in DEC/EC at 25 °C</td>
<td>1 X 10(^{-9}) ( \approx 1 X 10^{-10} ) (Na); 3 X 10(^{-9}) ( \approx 2 X 10^{-11} ) (Li)</td>
<td>[71]</td>
</tr>
<tr>
<td>( NaSn_2(PO_4)_3 ) (NASICON)</td>
<td>25 °C</td>
<td>6.03 X 10(^{-12})</td>
<td>[72]</td>
</tr>
<tr>
<td>( Na_2V_3(PO_4)_3@C)-B-doped</td>
<td>NaClO(_4) (0.8 M) at RT in (1:1; v/v) of DEC/EC</td>
<td>4.0 X 10(^{-14}) ( \approx 2.48 ) X 10(^{-13})</td>
<td>[73]</td>
</tr>
<tr>
<td>(NASICON)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( NaTi_2(PO_4)_3 )</td>
<td>NaCF(_3)SO(_3) (1 M) at RT in DMSO</td>
<td>1 X 10(^{-9}) ( \approx 10^{-12} )</td>
<td>[74]</td>
</tr>
<tr>
<td>( LiNi_{0.5}Mn_{0.5}O_2 );</td>
<td>LiPF(_6) (0.5 M) in PC/FEC (98:2; w/w); NaPF(_6) (0.5 M) at 25 °C in PC with FEC (2 wt.%)</td>
<td>7.7 X 10(^{-12}); 6 X 10(^{-13})</td>
<td>[75]</td>
</tr>
<tr>
<td>( Na_{0.44}MnO_2 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon fiber</td>
<td>LiPF(_6) (1 M) at 20 °C in DMC/EC</td>
<td>( \approx 10^{-10} )</td>
<td>[77]</td>
</tr>
<tr>
<td>( NaTi_2(PO_4)_3 ) (NASICON)</td>
<td>NaClO(_4) (1 M) at RT in DEC/EC (1:1; v/v) with FEC (3 wt.%)</td>
<td>2.0 X 10(^{-13})</td>
<td>[78]</td>
</tr>
<tr>
<td>( Na_{0.44}MnO_2 )</td>
<td>NaClO(_4) at 25 °C in (1:2; v/v) DMC/EC</td>
<td>5.75 X 10(^{-16}) ( \approx 2.14 ) X 10(^{-14})</td>
<td>[79]</td>
</tr>
<tr>
<td></td>
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<td></td>
</tr>
<tr>
<td>Graphene (Bilayer)</td>
<td>2 ( \approx 4) % 2-hydroxy-2-methylpropiophenone and LiTFSI at RT in BEMA:PEGMA (7:3)</td>
<td>10(^{-6}) ( \approx 7 X 10^{-5})</td>
<td>[80]</td>
</tr>
<tr>
<td>( P_2)-Na(<em>{0.66}Ti</em>{0.37}Cr_{0.63}O_2 )</td>
<td>NaClO(_4) in PC with FEC (2 %) at 25 °C</td>
<td>1 X 10(^{-12}) ( \approx 2 X 10^{-13} )</td>
<td>[81]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Graphite</td>
<td>LiPF(_6) (1 M) at 20 °C in DMC/EC</td>
<td>1.12 X 10(^{-10}); 1.35 X 10(^{-10}) (55 °C)</td>
<td>[82]</td>
</tr>
<tr>
<td>( NaTi_2(PO_4)_3@C ) (NASICON)</td>
<td>NaClO(_4) at RT in PC/EC</td>
<td>1.79 ( \approx 2.32 ) X 10(^{-10})</td>
<td>[83]</td>
</tr>
<tr>
<td>( Na_{3/8}V_2(PO_4)_3)–C (NASICON)</td>
<td>25 °C; NaPF(_6) in PC</td>
<td>2 X 10(^{-15}) ( \approx 6 X 10^{-13} )</td>
<td>[84]</td>
</tr>
<tr>
<td>( Li_{0.8}FePO_4; Na_{0.9}FePO_4 )</td>
<td>LiPF(_6) in DEC/EC; NaClO(_4) in DMC/EC at 25 °C</td>
<td>8.63 X 10(^{-17}); 6.77 X 10(^{-16})</td>
<td>[85]</td>
</tr>
</tbody>
</table>
Figure 1. Graphic representation of several electrode morphologies: (a) Insufficient storage kinetics of single crystal electrode (b) electronic transport via nanocrystalline particles with carbon black admixtures permitting for electrolyte access (c) Coated nanoparticles for optimized storage by conductive medium.

2.2 Cathode materials based on NASICON type

2.2.1 NASICON-type nanoparticles of Fe2(MoO4)3 wrapped with graphene

Sheng et al. [88] reported nanoparticles of Fe2(MoO4)3 (NASICON-type) wrapped through graphene for SIBs as an ultra-high rate cathode. To synthesize SIBs, nanoparticles of Fe2(MoO4)3 based on Na+ superionic conductor (NASICON) type is an utmost cathode material with a flat discharge plateau and capacious ion diffusion tunnels. Though, because of the long Na+ diffusion path and poor electron conductivity, the lethargic electrochemical kinetics bounds its additional advancement. The Fe2(MoO4)3 nanoparticle composite wrapped with graphene was synthesized by the microemulsion method followed by annealing. After 100 cycles at 10 ºC, the Fe2(MoO4)3 nanoparticle wrapped with graphene displays virtuous high-rate cycling stability up to 76% capacity retention and an ultra-high rate capability up to 64.1 mAh g⁻¹ at 100 ºC. The improved electrochemical concerts are ascribed to the inimitable composite structure having high electron conductivity and reduced ion diffusion distance. It was concluded that the nanoparticle of Fe2(MoO4)3 wrapped with graphene consumes the excessive latent meant for higher degree SIBs. The Fe2(MoO4)3 nanoparticle composite wrapped with graphene displays a significant capacity of 98.4 mAh g⁻¹ as a cathode material for SIBs with a flat voltage plateau [88].
2.2.2 NASICON-type materials based on Na$_3$V$_2$(PO$_4$)$_3$

Novikova et al. [89] synthesized NASICON-type materials having the compositions Na$_3$V$_{2-x}$Ni$_x$(PO$_4$)$_3$, Na$_3$V$_{2-x}$Cr$_x$(PO$_4$)$_3$, Na$_3$V$_{2-x}$Fe$_x$(PO$_4$)$_3$, and Na$_3$V$_{2-x}$Al$_x$(PO$_4$)$_3$ where x = 0.05, 0.03, 0.1, and 0. The outcomes determine that the doped material (5% Fe: Na$_3$V$_{1.9}$Fe$_{0.1}$(PO$_4$)$_3$) showed maximum electrical conductivity amongst the samples studied, having ~33 kJ/mol of activation energy at high-temperature conduction. Besides, for low-temperature conduction, the activation energy is decreased from 84 ± 2 to 54 ± 1 kJ/mol. At the elevated charge rate, the more porous material retains its high level of the theoretical capacity [89].

Zheng et al. [90] also described Na$_3$V$_2$(PO$_4$)$_3$ (NVP) type NASICON-based electrode material for SIBs. The remarkably high ion conductivity and distinct structural stability of the synthesized sodium salt of vanadium phosphate {Na$_3$V$_2$(PO$_4$)$_3$ (NVP)} interpreted it as an utmost auspicious conductor used for sodium storage. Therefore, via coating the vigorous materials thru downsizing the NVP particles, assimilation the NVP particle by ion doping strategy and many carbon materials, and with a conductive carbon layer, various actions have been adapted to upsurge the intrinsic electrical conductivity and surface of NVP. Additionally, to gain an improved consideration in the temperature range of −30 °C~225 °C on the sodium storage in NVP, four separate crystal structures, specifically β-NVP, γ-NVP, β’-NVP, and α-NVP. Furthermore, the authors gave an outline of current methods to augment the intrinsic electrical conductivity and surface electrical conductivity of NVP [90].

2.2.3 NASICON-type materials based on Na$_3$V$_2$(PO$_4$)$_2$F$_3$ and Na$_3$V$_2$(PO$_4$)$_3$

For SIBs, the NASICON materials, i.e., Na$_3$V$_2$(PO$_4$)$_2$F$_3$ and Na$_3$V$_2$(PO$_4$)$_3$ have resumed designate for electrochemical examination as proficient material for cathode by Song et al. [91]. The Na$_3$V$_2$(PO$_4$)$_2$F$_3$ has been synthesized by the insertion of fluorine through substituting limited PO$_4^{3-}$ groups in Na$_3$V$_2$(PO$_4$)$_3$. Significantly, to change the configuration of the ion including the quantity of varied Na sites, ions occupation, and for ions extraction, the species leads to different modifications, fluorine is proficient at partaking in structural development. Because of its strong ionicity, the (PO$_4$)$_2$ polyanion’s inductive effects can be enhanced by changing electronic cloud density underneath the consequences of molded F-V bond upon compositional atoms. These effects could restrain the redox pair energetics of transition metal ions from generating moderately high operating potentials. Predominantly, to upsurge achieved voltages through varying atomic surroundings, the replacement of fluorine intended for negative-charge anion or polyanion can be operative to advance the electrochemical possessions. Additionally, one
A clear couple of redox reaction peaks are accessible in CV (cyclic voltammetry) curves of Na$_3$V$_2$(PO$_4$)$_3$ while in CV curves of Na$_3$V$_2$(PO$_4$)$_2$F$_3$ two couples have come out [91].

2.2.4 NASICON-type materials of porous Na$_3$V$_2$(PO$_4$)$_3$ and NaTi$_2$(PO$_4$)$_3$

Zhang et al. [92] reported that due to their viable price benefits, SIBs grasp the high potential for grid-level energy storage devices. However, to empower high power and extended lifetime, contests persist in the advancement of appropriate conductor composites. Zhang et al. [92] synthesized the porous sodium salt of titanium phosphate (NaTi$_2$(PO$_4$)$_3$) and the sodium salt of vanadium phosphate (Na$_3$V$_2$(PO$_4$)$_3$) compounds intended to high rate cycling stability in cooperation with their electrochemical concerts. Owing to the upsurge thermal stability of the PO$_4^{3-}$ based anode and cathode materials, the Na$_3$V$_2$(PO$_4$)$_3$//NaTi$_2$(PO$_4$)$_3$ cells display simple production and wellbeing with 94% of capacity retention over 5000 cycles (ultralong cycle life), 80% efficiency of energy, and 85 mAh g$^{-1}$ of power at 2.4 A g$^{-1}$ based on cathode.

The NaTi$_2$(PO$_4$)$_3$ (NTP) and Na$_3$V$_2$(PO$_4$)$_3$ (NVP) composites have been produced by a scalable sol-gel method having a porous structure. Furthermore, these cells showed good concert retaining aluminum consistent with the current collector for the anode, though some enhancements must be required to attain improved power capability and energy efficiency of these kinds of current collector material [92].

2.2.5 A negative electrode of Mg$_{0.5}$Ti$_2$(PO$_4$)$_3$ based NASICON materials

The particles of Mg$_{0.5}$Ti$_2$(PO$_4$)$_3$ was synthesized by sol-gel synthesis process, which is a polyanion material coated with carbon and utilize for SIBs as the negative electrode materials. The material showed a precise capacity in the voltage gap of Na$^+$/Na$^0$ vs 0.01-3.0 V around 268.6 mAh g$^{-1}$. The material showed advanced rate capability in the NASICON based materials, at a current density of 5 A g$^{-1}$ having a specific capacity of 94.4 mAh g$^{-1}$ because of the fast diffusion of Na$^+$. Additionally, after 300 cycles, the retention capacity was achieved at 99.1%, signifying outstanding cycle stability.

On comparing with LIBs, Mg$_{0.5}$Ti$_2$(PO$_4$)$_3$ showed 629.2 mAh g$^{-1}$ of capacity ascribed to formation/decomposition of the SEI film in the voltage range of 0.01-3.0 V vs Li$^+$/Li$^0$ and the interfacial Li$^+$ storage. After the first release, the pristine particles of Mg$_{0.5}$Ti$_2$(PO$_4$)$_3$ became encapsulated into Li$_3$PO$_4$ in addition to solid electrolyte interphases (SEI) matrix and decayed to metallic Mg and Ti nanocrystals. The surface area of the material closely related to the capability of interfacial Li$^+$ storage, the specific capacity increases as an increase in the surface area. The sub-micron sized Mg$_{0.5}$Ti$_2$ showed a 600 mAh g$^{-1}$ capacity of Li$^+$ (PO$_4$)$_3$ electrode, which was comparable to the conversion reaction, for instance, NiO [93] and MoS$_2$ [94] and was considerably higher than other materials based
on the intercalation reaction such as TiO$_2$ [95] and graphite [96]. Through complementary
the mass ratio of the negative and positive conductors and regulating the working voltage
range, the full battery concert could be improved. To conclude, the Na$_{3.5}$Mg$_{0.5}$Ti$_2$(PO$_4$)$_3$
electrochemical disintegration was not perceived of the SIB cell because of the large
electrode polarization. The manufacturing of composite materials with carbon additives
and synthesis of nano Mg$_{0.5}$Ti$_2$(PO$_4$)$_3$ are some strategies utilized for the disintegration of
Na$_{3.5}$Mg$_{0.5}$Ti$_2$(PO$_4$)$_3$. In these types of strategies, a large Na$^+$ capacity could be obtained
thru taking benefit of the interfacial Na$^+$ storage mechanism [97].

2.2.6 Numerous other NASICON cathode materials

In addition to Na$_3$V$_2$(PO$_4$)$_2$F$_3$ (NVPF) and NVP there are various extra fascinating
materials like Fe$_2$(MoO$_4$)$_3$, Na$_3$Fe$_2$(PO$_4$)$_3$, Na$_2$TiFe(PO$_4$)$_3$, Na$_{1.5}$VOPO$_4$F$_{0.5}$, NaVPO$_4$F,
NaNbFe(PO$_4$)$_3$, and Na$_3$(VO$_{1-x}$PO$_4$)$_2$F$_{1+2x}$ also utilized as NASICON materials for SIBs
[57,59,98-105]. Inadequately, low sodium lodging capability showed by Na$_3$Fe$_2$(PO$_4$)$_3$,
which distributed only 45 mAh g$^{-1}$ of the lodging capability [106]. Similar problems are
faced by phosphates of a transition metal, for example, Ni, Mn, Cu etc. [58]. The
compound Fe$_2$(MoO$_4$)$_3$ which is of comprising of tetrahedral MoO$_4$ and octahedral FeO$_6$
consistent over corner distributing oxygen atoms is a monoclinic (P21/c) crystal structure
considered as more electro-active NASICON compounds. Because of structural and good
thermal stability, this compound proved as a capable cathode material for both Li as well
as Na ions [59,107-111]. An open tunnel is designed by enabling a robust structure
having three MoO$_4$ tetrahedra and two FeO$_6$ octahedra connected [103]. Two discharge
plateaus have been obtained on addition of two Na-ions at 2.55 V and 2.62 V as a typical
charge/discharge. Fu et al. [59] assumed the reduction of particle size to advance the
electrochemical concert of Fe$_2$(MoO$_4$)$_3$. Furthermore, to augment the electrochemical
concerts coating of graphene was also demonstrated [108,112]. Moreover, some other
NASICON compounds, for example, Na$_2$TiM(PO$_4$)$_3$ are similarly Na-active composites
where, M = Cr, Fe having dual transition metals consistent to Cr$^{2+}$/Cr$^{3+}$, Fe$^{2+}$/Fe$^{3+}$, and
Ti$^{3+}$/Ti$^{4+}$ redox processes. The redox procedures for M = Cr, Fe, two desodiation steps are
comprised, the first related to Cr$^{2+}$/Cr$^{3+}$ and Fe$^{2+}$/Fe$^{3+}$ value variations, and the second
corresponds to Ti$^{3+}$/Ti$^{4+}$. These NASICON materials need further optimization to attain
higher ionic conductivity and virtuous thermal steadiness to accomplish improved
electrochemical performances. For the deliberated NASICON cathode materials, all
appropriate figures and parameters of advantages are comprised in Table 2.
Table 2. Appropriate figures and parameters of advantages of NASICON cathode materials.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Capacities (mAhg$^{-1}$)</th>
<th>Morphology</th>
<th>Size (nm)</th>
<th>Capacity retention (%)</th>
<th>Cycle number</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$(MoO$_4$)$_3$</td>
<td></td>
<td>Thin film</td>
<td>200</td>
<td>80.8</td>
<td>100</td>
<td>[59]</td>
</tr>
<tr>
<td>Na$_3$V$_2$(PO$_4$)$_3$/CS</td>
<td>94, at 1 C</td>
<td>Nanowires (core-shell)</td>
<td>20–50</td>
<td>74</td>
<td>50</td>
<td>[113]</td>
</tr>
<tr>
<td>Na$_3$V$_2$(PO$_4$)$_3$@C@rGO</td>
<td></td>
<td>3D porous composites</td>
<td>50</td>
<td>64</td>
<td>10,000</td>
<td>[114]</td>
</tr>
<tr>
<td>Na$_3$V$_2$(PO$_4$)$_3$@C</td>
<td>104.3, at 0.5 C</td>
<td>Nanoparticles</td>
<td>40</td>
<td>99.6</td>
<td>50</td>
<td>[115]</td>
</tr>
<tr>
<td>Na$_3$V$_2$(PO$_4$)$<em>3$@C-B$</em>{0.38}$</td>
<td>87.1, at 0.2 C</td>
<td>Nanoparticles</td>
<td>100–800</td>
<td>81</td>
<td>50</td>
<td>[116]</td>
</tr>
<tr>
<td>Na$_3$V$_2$(PO$_4$)$_3$-F/C</td>
<td>103, at 0.1 C</td>
<td>Nanofibers</td>
<td>10</td>
<td>99.3</td>
<td>50</td>
<td>[117]</td>
</tr>
<tr>
<td>Na$_3$V$_2$(PO$_4$)$_3$@CNT-G</td>
<td>109, at 30 C; 82, at 100 C</td>
<td>3D foam</td>
<td>50–100</td>
<td>96</td>
<td>2000</td>
<td>[60]</td>
</tr>
<tr>
<td>Na$_3$V$_2$(PO$_4$)$_3$@AC</td>
<td>100.6, at 5 C</td>
<td>Nanoparticles</td>
<td>5</td>
<td>96.4</td>
<td>200</td>
<td>[118]</td>
</tr>
<tr>
<td>Na$_3$V$_2$(PO$_4$)$_3$F$_3$@C</td>
<td>126, at 0.1 C</td>
<td>Nanorods</td>
<td>200</td>
<td>92</td>
<td>50</td>
<td>[119]</td>
</tr>
<tr>
<td>Na$_3$V$_2$(PO$_4$)$_3$@C/G</td>
<td>86.5, at 40 C</td>
<td>3D porous composites</td>
<td>100</td>
<td>80</td>
<td>1500</td>
<td>[120]</td>
</tr>
<tr>
<td>Na$_3$V$_2$(PO$_4$)$_3$@C–N–CNT</td>
<td>93.8, at 0.2 C</td>
<td>NPs with CNT</td>
<td>100</td>
<td>92.2</td>
<td>400</td>
<td>[121]</td>
</tr>
<tr>
<td>C@Na$_3$V$_2$(PO$_4$)$_3$@pC</td>
<td>103, at 10 C</td>
<td>Double-shell nanospheres</td>
<td>20–40</td>
<td>80.5</td>
<td>1000</td>
<td>[122]</td>
</tr>
<tr>
<td>Na$_3$V$_2$(PO$_4$)$_3$F$_3$@PC</td>
<td>111, at 1.82 C</td>
<td>Porous nanoparticles</td>
<td>&lt;1000</td>
<td>98.2</td>
<td>90</td>
<td>[123]</td>
</tr>
<tr>
<td>Na$_3$V$_2$(PO$_4$)$_3$@C</td>
<td>110, at 10 C</td>
<td>3D nanofibers</td>
<td>20–80</td>
<td>95.9</td>
<td>1000</td>
<td>[124]</td>
</tr>
<tr>
<td>Na$_3$V$_2$(PO$_4$)$<em>3$@C-N$</em>{142}$</td>
<td>101.9, at 0.2 C</td>
<td>Porous particles</td>
<td>200</td>
<td>95.5</td>
<td>50</td>
<td>[125]</td>
</tr>
<tr>
<td>Na$_3$V$_2$(PO$_4$)$_3$F$_3$/PC</td>
<td>111.5, at 0.091 C</td>
<td>Nanoparticles</td>
<td>&lt;500</td>
<td>93</td>
<td>100</td>
<td>[126]</td>
</tr>
<tr>
<td>Na$_3$V$_2$(PO$_4$)$_3$@C@C-MK-3</td>
<td>115, at 1 C; 109, at 5 C</td>
<td>3D CMK-3</td>
<td>3</td>
<td>68</td>
<td>2000</td>
<td>[127]</td>
</tr>
<tr>
<td>Na$_3$V$_2$(PO$_4$)$_3$@MCNT</td>
<td>146.5, at 0.1 C</td>
<td>MCNT NCs</td>
<td>100</td>
<td>94.3</td>
<td>50</td>
<td>[128]</td>
</tr>
<tr>
<td>Na$_3$V$_2$(PO$_4$)$_3$F$_3$@AC</td>
<td>116, at ≈0.1 C</td>
<td>Nanoparticles</td>
<td>40–200</td>
<td>97.6</td>
<td>50</td>
<td>[129]</td>
</tr>
</tbody>
</table>

2.3 Anode materials based on NASICON-type

The usage of sodium metal is challenging due to safety motives to the extent that SIBs anodic materials are worried. Throughout the Na charge/discharge process, dendrites could be formed due to higher chemical reactivity than lithium metal. Amongst four kinds of storage mechanisms, one has to differentiate for an electrode, i.e. interfacial storage and conversion reaction. This was comprehended in relevant materials, for
example, Na-alloys, single phase absorption, ionic in addition to covalently bonded composites, phase-transition, which is analogous to LIB [130-136].

In comparison to Li-based batteries, multi-phase reactions are more probable due to the typically subordinate solubility of Na. NASICON type materials, for example, sodium salt of vanadium phosphate (Na$_3$V$_2$(PO$_4$)$_3$), sodium salt of zirconium phosphate {NaZr$_2$(PO$_4$)$_3$} (NZP), and sodium salt of titanium phosphate {(NaTi$_2$(PO$_4$)$_3$) (NTP)} distinct towards transitional metal sulfides/oxide including conversion reactions with high rate capabilities, are deliberated as utmost capable anodes for SIB.

Additionally, as anode materials for SIBs, the rGO-CNT modified sodium salt of vanadium phosphate (Na$_3$V$_2$(PO$_4$)$_3$) compounds have been applied by Zhu et al. [137] having capacity retention ratio of 77% at 10 °C. Here, mainly the property, preparation, and concert of NZP, NTP has been discussed and considered as negative electrodes in NASICON type materials.

### 2.3.1 NaTi$_2$(PO$_4$)$_3$ (NTP) type anode materials

NTP is a triclinic NASICON variant (P1) which is frequently used SIB anode material [137-139]. NTP shaped on Ti$^{3+}$/Ti$^{2+}$, and Ti$^{4+}$/Ti$^{3+}$ valence variations divulge two discharge plateaus between 0 V and 3 V at 2.1 V and 0.4 V. The strategy above using conductive agents is suitable as NTP, NVP particles labor under inadequate electrical conductivity, for example, carbon shell, graphene, and CMK-3. Similarly, particle size reduction is true. The 3D graphene networks entrenching NTP nanoparticles (NTP@GN) has been synthesized using a hydrothermal method. Also, allowing fast charge transport and transfer, the porous NTP nanoparticles having particle size around ≈100 nm is uniformly dispersed inside the graphene nanonetwork, which is preserved throughout cycling. After 200 cycles, the NTP@GN composites delivered a high capacity and high retention ratio (93%) at 109 mAh g$^{-1}$ of capacity. Additionally, a homogeneously spread CMK-3 (5 nm) matrix in CMK-3 channels has been utilized by Zhang et al. [140]. At 0.2 C, about 100 mAh g$^{-1}$ of the attained NTP@CMK-3 composites distributed good cycling concert with an alterable capacity between 1.5 V and 3 V. The carbon-coated NVP (NTP@C) composite has been synthesized where titanium isopropoxide is used as titanium source and citric acid as a carbon source [83]. The NTP nanoparticles have virtuous crystallinity having two charge/discharge plateaus and a 7 nm carbon layer exhibited by the ensuing NTP@C composites.

### 2.3.2 NaZr$_2$(PO$_4$)$_3$ (NZP) type anode materials

The sodium salt of zirconium phosphate (NaZr$_2$(PO$_4$)$_3$) has been produced and electrochemically examined as a fascinating NASICON-type anode material by Jiao et al.
The octahedral ZrO$_6$ and tetrahedral PO$_4$ structures are composed to synthesize NaZr$_2$(PO$_4$)$_3$ in which ZrO$_6$ behave as the host for Na$^+$ ions. However, over PO$_4$-ZrO$_6$ polyhedral tunnels, a rapid gesture of the Na$^+$-ions permitted by the open structure. The XRD patterns were utilized to confirm the disparity of the Na content. Throughout charge/discharge processes, the diverse stage conditions of mono and trisodium salt of zirconium phosphate {\{NaZr$_2$(PO$_4$)$_3$ and Na$_3$Zr$_2$(PO$_4$)$_3$\}} has been signified. The two lattice spacings of 6.33 Å and 4.40 Å demonstrated using HRTEM, corresponded to the hkl values of (012) and (110) planes. Through the charge/discharge process of NZP the Na$_{1-x}$Zr$_2$(PO$_4$)$_3$ converted into Na$_{3-y}$Zr$_2$(PO$_4$)$_3$ using redox reactions where (0 < x < 1, 0 < y < 1). Due to stable coulombic efficiency [141], with steady cycling and rapid kinetics concert, the NZP compounds considered as anode materials for SIB.

2.3.3 Numerous other NASICON anode materials

For activation in full batteries, amorphous Sn, Sb, P, or carbon needed pre-sodiation because these are non-Na materials [142]. This causes pronounced irreversible capacity losses and devours much of sodium to produce steady layers of SEI. In addition to NZP (NaZr$_2$(PO$_4$)$_3$) and NTP (NaTi$_2$(PO$_4$)$_3$) compounds, some other anode composites, such as, mono- and trisodium salt of vanadium phosphate (Na$_3$V$_2$(PO$_4$)$_3$), mixed salt of manganese and titanium phosphate (Na$_3$MnTi(PO$_4$)$_3$), sodium salt of tin phosphate (NaSn$_2$(PO$_4$)$_3$), and sodium salt of titanium phosphate (Na$_3$Ti$_2$(PO$_4$)$_3$) should be mentioned consistent with NASICON based materials. For instance, the mono- sodium salt of vanadium phosphate (NaV$_2$(PO$_4$)$_3$) materials in the non-aqueous electrolyte as anodes are of more importance [143-146]. Furthermore, Jian et al. [147] demonstrated Na$_3$V$_2$(PO$_4$)$_3$ with deep sodiation processes at 0.3 V and 1.6 V thru synthesis of tetra- and penta- sodium salt of vanadium phosphate \{Na$_4$V$_2$(PO$_4$)$_3$ and Na$_5$V$_2$(PO$_4$)$_3$\}, respectively. At 11.7 mAh g$^{-1}$ (0.1 C), Na$_3$V$_2$(PO$_4$)$_3$ exhibited a higher reversible measurement of 149 mAh g$^{-1}$ and virtuous rate measurements [147]. The anode materials mentioned above could be practical to accumulate full cells originated on NASICON-type electrodes [148]. The sodium salt of vanadium and titanium phosphate, respectively \{Na$_3$V$_2$(PO$_4$)$_3$, NaTi$_2$(PO$_4$)$_3$\} and are accumulated utilizing Na$_2$SO$_4$ (1 M) aqueous electrolyte solution to form a full cell and the voltage-profiles distributing an over-potential of 1.3 V. In aqueous electrolyte, Na$_3$MnTi(PO$_4$)$_3$ considered as both material i.e. cathode and anode which is also another characteristic example of NASICON full cell [149]. Deprived of seeming polarization throughout cycles, around 1.4 V, a rescindable competence of 57.9 mAh g$^{-1}$ has been used for characterization of the charge/discharge processes centred at 0.5 C. Various other NASICON compositions have been prepared with Ti, Ni, Mn etc. For the deliberated anode materials, all appropriate figures of virtues and parameters are listed in Table 3. Masquelier’s group recently reported NVP cell in which a NASICON
solid electrolyte was utilized to detach the cathode and anode [149]. However, for reasonable performance, the elevated temperature was necessary, demonstrates the difficulty of all-solid-state batteries.

2.4 Commercial prospects of NIB technologies

Diverse NIB chemistries are existence established as by LIBs; materials for electrolytes, cathodes, and anodes are all existence examined minutely. About specific materials, this section précises the effort in emerging fuel-cell technologies. Four groups may be characterized for NIBs through the most cathode and anode materials. For cathodes: polyanionic compounds, layered $O_3$, Prussian blue analogs, and layered $P_2$; For anodes: carbonaceous, phosphoric, alloy, and metal sulfide/oxide comprised in Table 3. The layered oxide cathode cells in comparison to the polyanion systems, displayed advanced reversible capacities. When extra sodium inserted into the system, the pre-sodiated anode cells exhibited higher reversible specific capacities. Since 2014, numerous vital NIB
commercial improvements have been displayed thru numerous corporations worldwide. The O₃-type NaNi₀.₃Fe₀.₄Mn₀.₃O₂ and hard carbon anode were demonstrated, which was a prototype pouch cell of capacity around 650 mAh g⁻¹ [60]. The SHARP labs of America demonstrated a hard carbon battery vs a 3 V Prussian white cathode in 2015. This showed that the rate of competence was restricted via a 30% first-cycle loss and the hard carbon anode [61]. Faradion established a solid carbon anode and a cathode cell based on Ni containing layered oxide {126 watt-hours (Wh kg⁻¹)} with 300 cycles. In 2016, a solid carbon anode of sodium nickelate oxide doped with tin demonstrated by SHARP labs of Europe. These materials exhibited uppermost reported volumetric energy density in NIB up to now. The values of these high energy densities with a 3.4 and a 4.2 Ah pouch cell were found up to 211 and 250 Wh L⁻¹.

Conclusions

NASICON-type composite materials have remarkable characteristics of excellent thermal stability, high ionic conductance, and steady structural framework, which can apply in various areas, like electrodes for gas sensors, membrane for lithium-oxygen batteries, Na-ion batteries, solid electrolytes, fuel cells and Li-ion batteries. Previously, to attain elevated performance SIBs, immense development has been completed in the growth of electrode materials based on NASICON-type. This chapter focused on design principles to optimize the functions of electrode materials based on NASICON-type and offered advantages and disadvantages of these materials. Electrochemical properties and synthesis are thoroughly interlinked because morphology is imperative. For efficient and reliable anode and cathode, the NASICON system presents an exceedingly constructive and multipurpose platform. Currently, to defeat all the discussed materials is within the range of vision display precise short-comings but a variety of potential. Owing to lower potential gaps the energy density of NIBs demonstrates no benefits to LIBs, in so far as the elevated standard functioning potentials of electrode materials based on NASICON-type as an anode, which may be a tentative obstruct for useful relevance. Though, using other anode materials, this discomfited situation can be improved with properties of subordinate discharge potential. Because of the comparatively lower energy density and higher ionic conductivity than other energy-oriented materials, the NASICON-based vigorous materials contrast to another sodium/lithium-based cathode are concerned with additional power materials. In various labs and research, the solid batteries made of materials based on NASICON type are under development, these consents highly prevailing Na-electrolytes due to the higher ionic conductance of materials based on NASICON-type.
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