RSC Advances

Enhanced sodium ion conductivity in Na₃VS₄ by P-doping

Yu He,a Fengqi Lu,⁎b and Xiaojun Kuang c,a

All-solid-state sodium-ion batteries are promising candidates for renewable energy storage applications, owing to their high safety, high energy density, and the abundant resources of sodium. The critical factor for an all-solid-state battery is having a sodium solid electrolyte that has high Na ion conductivity at room temperature and outstanding thermal stability, low flammability, and long battery lifespan. Herein, a new Na ion solid-state electrolyte, Na₃VS₄, is prepared by a solid state reaction. It shows conductivity of ~1.16 × 10⁻⁸ to 1.46 × 10⁻⁶ S cm⁻¹ from 25 to 100 °C. The sodium ion conductivity was enhanced to ~1.49 × 10⁻⁷ to 1.20 × 10⁻⁵ S cm⁻¹ through P substitution for V in the composition Na₃P₀.₁V₀.₉S₄. Such sodium ion conduction enhancement could be attributed to P substitution for V leading to a wider Na migration path and the generation of sodium vacancies.

Sulfur-based Na-ion solid electrolytes offer promising room temperature conductivities. The tetragonal phase of Na₃PS₄ had been known as a sodium conductor for more than 20 years.¹¹ Na₃PS₄ has gained renewed attention since Hayashi et al. synthesized a room temperature stable glass-ceramic phase, which showed a Na ionic conductivity of 2 × 10⁻⁴ S cm⁻¹ and subsequently increased to 4.6 × 10⁻⁴ S cm⁻¹ by using high purity raw materials.¹²⁻¹⁵ The conductivity of (1 − x)Na₃PS₄-xNa₄SiS₄ pseudo-binary system could achieve as high as 7.4 × 10⁻⁴ S cm⁻¹ at x around 0.0629.¹⁶⁻¹⁷ The Cl-doped tetragonal Na₃PS₄ (ref. 18) (t-Na₂₉.₅₇₃⁷S₃₉.₅₇₁₇Cl₀.₆₂₅) solid electrolyte displayed a Na ion conductivity exceeded 1 × 10⁻³ S cm⁻¹ at room-temperature. Moreover, the cell parameters had played an important role for Na ion transport, such as Na₃PSe₄ (ref. 19) and Na₃SbS₄,²⁰ which owned larger cell parameters than Na₃PS₄, their ionic conductivity increased to 1.16 × 10⁻³ S cm⁻¹ and 3 × 10⁻⁷ S cm⁻¹, respectively. Recently, Luo and Wang reported a Na-ion solid-state electrolyte of Na₃P₀.₆₆₂₆As₀.₃₄S₄, which had a high ionic conductivity of 1.46 × 10⁻⁴ S cm⁻¹. Richards et al. reported a family of Na₁₀MP₃S₁₂ (M = Sn, Ge, and Si) with a high ionic conductivity of 4 × 10⁻⁴ S cm⁻¹ for Na₁₀SnP₃S₁₂, and also predicted a super high ionic conductivity of 10.28 × 10⁻⁴ S cm⁻¹ for Na₁₀SiP₃S₁₂ based on first-principles simulations.²¹⁻²² Nonetheless, the sodium superionic conductors are still rate and their room-temperature ionic conductivities can’t satisfy the actual needs. Looking for new solid-state sodium ion conductor is highly anticipated for all-solid-state rechargeable sodium ion batteries.

Na₃VS₄ crystals were reported more than twenty years ago,²³ which adopted a tetragonal structure closely related to the Na₃PS₄.¹¹ However, there is no attention on its sodium ionic conductivity so far. In this study, Na₃VS₄ was synthesized by solid state method, which owns sodium ionic conductivity of

Introduction

There is growing demand for high performance rechargeable batteries used in large-scale energy storage, including electric vehicles and backup storage at individual houses and large-scale solar and wind farms.¹ To date, rechargeable battery technology is dominated by lithium ion batteries, but the geographically constrained Li resources will ultimately push up prices, in turn limiting their application potential in large-scale energy storage. Moreover, from a battery producer viewpoint, principal importance is always given to material abundance and low cost when designing an electrode, i.e., sodium, which is an abundant element in nature while lithium is not. As one classic ion battery, the sodium ion battery has risen to prominence as a key supplement for large-scale energy storage systems.² However, severe safety issues also exist in sodium ion batteries using organic liquid electrolytes, because of extremely high reactivity of volatile sodium metal and flammable organic liquid electrolytes.³⁻⁶ Among various methods for improving the safety of electrolytes, the inorganic solid electrolytes have been proposed for development of thermally stable electrolytes.⁷ Compared with traditional organic electrolytes, solid state electrolytes have excellent thermal stability,⁸ low flammability, and potentially better battery life due to the increased electrochemical stability.⁹⁻¹⁰ Based on these advantages, solid-state electrolytes are considered to be the most promising components for next generation secondary batteries.

¹College of Chemistry and Bioengineering, Guilin University of Technology, Guilin 541004, P. R. China
²Guangxi Key Laboratory of Optical and Electronic Materials and Devices, MOE Key Laboratory of New Processing Technology for Nonferrous Metal and Materials, College of Materials Science and Engineering, Guilin University of Technology, Guilin 541004, P. R. China. E-mail: lufengqi@glut.edu.cn
~1.16 × 10⁻⁸ to 1.46 × 10⁻⁶ S cm⁻¹ from 25 °C to 100 °C. In order to improve its sodium ionic conductivity, P-doped Na₃VS₄ (i.e. Na₃PₓV₁₋ₓS₄, 0 ≤ x ≤ 0.2) was prepared, which resulted in higher Na-ion conductivity of ~1.49 × 10⁻⁷ to 1.20 × 10⁻⁵ S cm⁻¹ from 25 °C to 100 °C on composition x = 0.1.

**Experimental section**

**Synthesis**

Na₃PₓV₁₋ₓS₄ (0 ≤ x ≤ 0.2) electrolytes were prepared by solid-state reaction in vacuum. The stoichiometric amounts of Na₃S (Aladdin, >95%), P₂S₅ (Aladdin, 99%), and V (Aladdin, 99.99%) were well-mixed and ground with an agate mortar and pestle for one hour. Then, the mixture powder was vacuum-sealed in a quartz tube and heated at 500 °C for 6 h with a heating or cooling rate of 2 °C min⁻¹. All the processes were carried out in a high purity argon-filled glove box with H₂O and O₂ below 0.1 ppm.

**Materials characterization**

The X-ray diffraction (XRD) data of as-synthesized samples were collected using a PANalytical X’pert Powder X-ray diffractometer equipped with a Cu Kα radiation operating at an accelerating voltage of 40 kV and current of 40 mA. For Rietveld refinement, the data was acquired in the 2θ range of 10–80° with 0.0208° min⁻¹. For all the XRD measurements, to avoid any undesirable influence of air exposure, the as-obtained powders were sealed in an air-tight container with Kapton tape in an argon-filled glove box. The Rietveld refinements of the XRD data were carried out using Topas-Academic software. Raman scattering measurements were performed using DXR Raman Microscope with a 532 nm excitation source. In order to avoid any undesirable influence of air exposure, the as-obtained powders were sealed in an air-tight quartz box.

**Electrochemical tests**

The alternate current (AC) impedance spectroscopy measurements were performed by using a Solartron SI1260 impedance/gain-phase analyzer over a temperature range from 106 to 10⁻⁴ s⁻¹. The pellets (ϕ 6 mm) for AC impedance spectroscopy measurements were pressed from powders at 1000 MPa. The density of the pressed pellet was about 2.14 g cm⁻³, and achieved a theoretical density of 90%. Platinum foil was placed on both sides of the pellets as electrodes and current collectors. Platinum wire was attached to both sides as current collectors in a cell. The electrochemical stability of as-obtained sample with metallic sodium was determined via linear sweep voltammograms (LSV) of the Na/Na₃VS₄/Pt and Na/Na₃PₓV₁₋ₓS₄/Pt cells at a scan rate of 0.2 mV s⁻¹ from 1 to 6 V at room temperature. To determine electronic conductivity, potentiostatic direct current (DC) polarization measurements were performed on Pt/Na₃VS₄/Pt and Pt/Na₃PₓV₁₋ₓS₄/Pt cells by using a Solartron SI1287 electrochemical interface at 25 °C.

**Results and discussion**

The crystalline phase of as-synthesized samples by solid-state reaction were characterized by XRD. The XRD patterns were shown in Fig. 1, the halo patterns from 10° to 30° reflected from the polyimide film. As shown in Fig. 1a, the major diffraction peaks of Na₃VS₄ could index in tetragonal system with the space group P421c (space group no. 114)²⁴ beside some impurities, such as V₂O₅, S. The XRD data of Na₃VS₄ was also analyzed with Rietveld refinement (Fig. 1b). The fitting was satisfactory with rather low factors of R_{wp} ~ 4.98% and R_{P} ~ 3.61%. The cell parameters are a = b = 13.5246(1) Å and c = 7.9468(4) Å, with a unit volume of 1449.4(1) Å³. According the Rietveld refinement results, the content of V₂O₅ and S was 2.62 wt% and 6.78 wt%, respectively. Detailed structural informations, including the atomic parameters determined from Rietveld refinement, were listed in Table 1. After P-doping, the Na₃PₓV₁₋ₓS₄ sample could get a single phase (Fig. 1a), however, it exists a second phase of Na₃PS₄ in Na₃PₓV₁₋ₓS₄ (Fig. 1a and d). This indicate that the solid-solution in Na₃V₁₋ₓS₄/Pt was rather small. The Rietveld refinement of Na₃PₓV₁₋ₓS₄ with tetragonal Na₃VS₄ structure model was shown in Fig. 1c. The refined profiles fitted well the observed data, which converged to R_{wp} ~ 5.03% and R_{P} ~ 3.68%. The refined structural data and refinement parameters were listed in Table 2. The ratio of V/P is 0.88(5)/0.12(5) from the result of Rietveld refinement, which is agreed with the normal composition. The unit cell parameters obtained from the Rietveld refinement are a = b = 13.5051(7) Å, c = 7.9468(4) Å, V = 1449.4(1) Å³, which is a little less than those of Na₃VS₄. The compared cell parameters were given in Table 3. Due to the ionic radius of P⁵⁺ (0.29 Å) is smaller than that of V⁵⁺ (0.46 Å), P doping reduces the unit cell parameters.

Fig. 2 shows the Raman spectrum of Na₃VS₄ and Na₃PₓV₁₋ₓS₄ at room temperature. The broad peak located at 450 cm⁻¹ derived from the quartz box, and the peaks situated at about 490, 600 and 800 cm⁻¹ could assign to the V–S or V/P–S vibrations of the isolated of VS₄³⁻ or V/P₅S₄³⁻ group, verifying the successful formation of VS₄³⁻ or V/P₅S₄³⁻ group.¹²,²⁹ The crystal structure of tetragonal Na₃VS₄ viewed along c axes is given in Fig. 3a. The crystallographic structure unit cell can be simply described as consisting of isolated VS₄³⁻ tetrahedral groups separated by sodium cations. In unit cell, the Na₁, Na₂, Na₃, Na₄ atoms sit on 4d, 4e, 8e, 8e Wyckoff sites, V atoms locate at 8e sites and S atoms situate in 8e Wyckoff sites. The V–S distance are 2.38(1) Å (V–S₁), 2.28 Å (V–S₂), 2.37(1) Å (V–S₃), 2.36(1) Å (V–S₄) and the S–V–S angles are 104.3° (S₃–V–S₁), 115.4° (S₂–V–S₁), 102.3° (S₃–V–S₂), 111.3° (S₃–V–S₄), 114.5° (S₃–V–S₁), 108.8° (S₂–V–S₄). In the crystal structure, Na atoms sit on 4d (Na₁), 4e (Na₂), 8e (Na₃), 8e (Na₄) Wyckoff sites with different coordination environments (Fig. 3b), which are six-coordination for Na₁, eight-coordination for Na₂, six-coordination for Na₃ and seven-coordination for Na₄, respectively. Especially, Na₂ atom connects to eight sulfur atoms and from an anion framework, all of these Na₂ ion diffusion channels are constructed along mutually perpendicular paths (inset in the Fig. 3a). This anion framework is body-centered cubic.
framework, which benefits Na ion diffusion. This phenomenon similar to Gerbrand Ceder and co-workers proposed design principles for superionic conductors, they suggested that the body-centered cubic frameworks allow the migration of ions with a lower activation barrier than in other close-packed frameworks, thus resulting in fast ion diffusion. Moreover, because of the ionic radius of P5+ less than the V5+, the bond length of V/P—S is shorter than that of V—S (Fig. 3c). Also, as comparing in Table 4, the average bond length of Na2—S in Na3V0.5P0.5S4 (3.60(6) Å) was larger than that of Na3VS4 (3.51(7) Å), indicating that sulfur anion channels in Na3P0.1V0.9S4 were

| Table 1 | The final refined structural parameters of Na3VS4<sup>a</sup> |
|---------|-----------------------------|
| Atom    | Site | x   | y   | z   | Occupancy | B<sub>iso</sub> (Å<sup>2</sup>) |
| Na1     | 4d   | 0   | 0.5 | 0.5314(26) | 1 | 0.9(5) |
| Na2     | 4c   | 0.5 | 0.5 | 0.7260(29) | 1 | 0.9(5) |
| Na3     | 8e   | 0.7528(13) | 0.5468(10) | 0.8531(16) | 1 | 0.9(5) |
| Na4     | 8e   | 0.7544(13) | 0.8004(9) | 0.9030(20) | 1 | 0.9(5) |
| V1      | 8e   | 0.0100(5) | 0.7409(5) | 0.7849(9) | 1 | 2.6(2) |
| S1      | 8e   | 0.6806(7) | 0.5051(9) | 0.5262(12) | 1 | 1.2(3) |
| S2      | 8e   | 0.8600(7) | 0.6853(7) | 0.6699(13) | 1 | 1.2(3) |
| S3      | 8e   | 0.6069(7) | 0.9049(8) | 0.7042(15) | 1 | 1.2(3) |
| S4      | 8e   | 0.5805(8) | 0.6409(9) | 0.8972(13) | 1 | 1.2(3) |

<sup>a</sup> Space group: P4<sub>2</sub>1c, a = b = 13.5051(5) Å, c = 7.9467(4) Å, V = 1449.5(1) Å<sup>3</sup>.

| Table 2 | The final refined structural parameters of Na3P0.1V0.9S4<sup>a</sup> |
|---------|-----------------------------|
| Atom    | Site | x   | y   | z   | Occupancy | B<sub>iso</sub> (Å<sup>2</sup>) |
| Na1     | 4d   | 0   | 0.5 | 0.5606(19) | 1 | 1.7(2) |
| Na2     | 4c   | 0.5 | 0.5 | 0.7189(19) | 1 | 1.7(2) |
| Na3     | 8e   | 0.7580(9) | 0.5477(7) | 0.8339(13) | 1 | 1.7(2) |
| Na4     | 8e   | 0.7577(9) | 0.7970(7) | 0.9361(15) | 1 | 1.7(2) |
| V1/P1   | 8e   | 0.0101(3) | 0.7347(3) | 0.7811(5) | 0.88(5)/0.12(5) | 0.2(2) |
| S1      | 8e   | 0.6860(5) | 0.5140(5) | 0.5226(9) | 1 | 0.8(1) |
| S2      | 8e   | 0.8748(5) | 0.6877(5) | 0.6752(10) | 1 | 0.8(1) |
| S3      | 8e   | 0.6129(5) | 0.8929(5) | 0.6967(12) | 1 | 0.8(1) |
| S4      | 8e   | 0.5744(6) | 0.6609(6) | 0.8843(8) | 1 | 0.8(1) |

<sup>a</sup> Space group: P4<sub>2</sub>1c, a = b = 13.5051(5) Å, c = 7.9467(4) Å, V = 1449.5(1) Å<sup>3</sup>.

| Table 3 | The cell parameters of Na3VS4 and Na3P0.1V0.9S4 |
|---------|-----------------------------|
| Composition | a/b (Å) | c (Å) | V (Å<sup>3</sup>) |
| Na3VS4    | 13.5246(1) | 7.9500(7) | 1454.1(2) |
| Na3P0.1V0.9S4 | 13.5051(5) | 7.9467(4) | 1449.5(1) |
larger than the sulfur anion channels in Na₃VS₄. The larger channel reduced the force between sodium and sulfur, which is beneficial for Na ion diffusion.

The conductivity of pressed pellets of Na₃VS₄ and Na₃V₀.₉P₀.₁S₄ were evaluated by AC impedance spectroscopy, which were conducted in the frequency range from 10⁶ Hz to 0.1 Hz at 25–100 °C. The Nyquist plots of the impedance spectra of Na₃VS₄ and Na₃P₀.₁V₀.₉S₄ were shown in Fig. 4a and b, respectively. The impedance spectra both of Na₃VS₄ and Na₃P₀.₁V₀.₉S₄ contained a semicircle in the high-frequency region, which became smaller with increasing temperature. In the low frequency region, the semicircle segments follow a Warburg-type impedance, which is associated with capacitive behavior and similar to the blocking electrodes.

### Table 4
The bond length of Na₂–S in Na₃VS₄ and Na₃V₀.₉P₀.₁S₄

|            | Na₃VS₄ Length (Å) | Na₃V₀.₉P₀.₁S₄ Length (Å) |
|------------|-------------------|---------------------------|
| Na₂–S₁(C₂) | 3.15(1)           | 3.25(1)                   |
| Na₂–S₁(C₂) | 2.91(1)           | 2.98(1)                   |
| Na₂–S₄(C₂) | 2.58(1)           | 2.69(1)                   |
| Na₂–S₄(C₂) | 5.41(1)           | 5.48(1)                   |
| hL         | 3.51(6)           | 3.60(7)                   |

The conductivity of pressed pellets of Na₃VS₄ and Na₃V₀.₉P₀.₁S₄ were evaluated by AC impedance spectroscopy, which were conducted in the frequency range from 10⁶ Hz to 0.1 Hz at 25–100 °C. The Nyquist plots of the impedance spectra of Na₃VS₄ and Na₃P₀.₁V₀.₉S₄ were shown in Fig. 4a and b, respectively. The impedance spectra both of Na₃VS₄ and Na₃P₀.₁V₀.₉S₄ contained a semicircle in the high-frequency region, which became smaller with increasing temperature. In the low frequency region, the semicircle segments follow a Warburg-type impedance, which is associated with capacitive behavior and similar to the blocking electrodes. The
linear spike in the low-frequency region indicates Na$_3$VS$_4$ and Na$_3$P$_{0.1}$V$_{0.9}$S$_4$ were typical ionic conductor.

The Nyquist plot of Na$_3$P$_{0.1}$V$_{0.9}$S$_4$ at 25 °C (Fig. 4c) comprised bulk, grain boundary and electrode polarization. The high-frequency semicircle is characterized by a capacitance about $3 \times 10^{-11}$ F cm$^{-1}$ and could be attributed to ion transport in the crystalline and crystalline grains.$^{31}$ The electrode response was a Warburg-type spike characteristic of ion conductor. The total ionic conductivity ($\sigma_t$) could be calculated according to the formula:$^{31}$

$$\sigma = \frac{R}{L \cdot S}$$  \hspace{1cm} (1)

where $R$ is the total resistance, which could be gained from the Nyquist plot, $L$ is height of pellet, $S$ is the contact area. Arrhenius plots of the total ionic conductivity $\sigma$ for Na$_3$VS$_4$ and Na$_3$P$_{0.1}$V$_{0.9}$S$_4$ were depicted in Fig. 3d.

The linear dependence of log $\sigma_t$ versus $1/T$ follows the Arrhenius law and indicates phase stability over the given temperature range. As shown in the Table 5, the total ionic conductivity of Na$_3$VS$_4$ located in the range from $1.16 \times 10^{-8}$ S cm$^{-1}$ at 25 °C to $1.46 \times 10^{-8}$ S cm$^{-1}$ at 100 °C. However, the total ionic conductivity of Na$_3$P$_{0.1}$V$_{0.9}$S$_4$ placed $1.49 \times 10^{-7}$ S cm$^{-1}$ at 25 °C to $1.20 \times 10^{-5}$ S cm$^{-1}$ at 100 °C, which almost one order of magnitude higher than those of Na$_3$VS$_4$.

The activation energy $E_a$ for the sodium-ion conductor is determined from the slope of the linear Arrhenius plot using below equation:$^{32}$

$$\sigma_t = A \exp(-E_a/k_B T)$$  \hspace{1cm} (2)

where $\sigma_t$ is the total ionic conductivity, $A$ is the pre-exponential parameter, $T$ is absolute temperature, $E_a$ is the activation energy, and $k_B$ is the Boltzmann constant. The calculated activation energy of Na$_3$VS$_4$ is 0.65 eV, while it is 0.54 eV for Na$_3$P$_{0.1}$V$_{0.9}$S$_4$. The lower activation energy of Na$_3$P$_{0.1}$V$_{0.9}$S$_4$ than that of Na$_3$VS$_4$ indicated that the diffusion rate of sodium ions in Na$_3$P$_{0.1}$V$_{0.9}$S$_4$ is higher than those of Na$_3$VS$_4$ leading to higher conductivity.

Compared with Na$_3$VS$_4$, the P-doping Na$_3$P$_{0.1}$V$_{0.9}$S$_4$ showed higher Na ionic conductivity. Through P substitution for V on Na$_3$P$_{0.1}$V$_{0.9}$S$_4$ composition, it could decrease the size of V/PS$_4$$^{3-}$ tetrahedra and enlarge some sulfur anion channels. From the Rietveld refinement of Na$_3$P$_{0.1}$V$_{0.9}$S$_4$ data, the occupancy of Na$^2$ sites contains 92% Na plus 8% vacancies rather than full occupancy of Na. Recently, theoretical investigations on both Na$_3$PS$_4$ (ref. 14) and Na$_3$PSe$_4$ (ref. 19) revealed that a defect-driven diffusion mechanism (either Na ion interstitial or Na...
Na3VS4 has a transference number for sodium ions accordingly derived by favorable features, P doping Na3V0.9P0.1S4 gets higher Na ion minor electrons and/or holes (conductivity.

Table 5  Total ionic conductivity of Na3VS4 and Na3P0.1V0.9S4

| Composition | 25 °C (S cm⁻¹) | 40 °C (S cm⁻¹) | 60 °C (S cm⁻¹) | 80 °C (S cm⁻¹) | 100 °C (S cm⁻¹) |
|-------------|----------------|----------------|----------------|----------------|-----------------|
| Na3VS4      | 1.16 × 10⁻⁸    | 3.11 × 10⁻⁸    | 1.07 × 10⁻⁷    | 4.23 × 10⁻⁷    | 1.46 × 10⁻⁶     |
| Na3P0.1V0.9S4| 1.49 × 10⁻⁷    | 3.14 × 10⁻⁷    | 8.30 × 10⁻⁷    | 2.63 × 10⁻⁶    | 1.20 × 10⁻⁵     |

To evaluate the exactly contribution of the electronic contribution to the total conductivity in the Na3VS4 and Na3P0.1V0.9S4 electrolytes, potentiostatic (0.5 V was used in the present work) DC measurements were carried out on Pt/Na3VS4/Pt and Pt/Na3P0.1V0.9S4/Pt cells at 25 °C. The electronic conductivity curves were displayed in Fig. 5a and b. When the measurement was performed, as there are no external sources for Na⁺ ions, the electrodes are therefore blocking for Na⁺ ions, and the conductivity at steady stage under a DC voltage could be ascribed to the electronic conduction. According to the chronocamperometric curves, the electronic resistance can calculate from the formula R = U/I at steady stage, and then according to eqn (1) get the electronic conduction. The calculated values of σ(e-h) are about 8.60 × 10⁻⁹ and 1.76 × 10⁻⁸ S cm⁻¹ for Na3VS4 and Na3P0.1V0.9S4, respectively. Therefore, the calculated transport number of sodium ions (tNa⁺) are about 0.3 for Na3VS4 and 0.9 for Na3P0.1V0.9S4 according to tNa⁺ = σNa⁺/σe, indicating that P-doping could greatly improve the transport number of sodium ions leading to higher total conductivity.

The electrochemical stability of Na3VS4 and Na3P0.1V0.9S4 with metallic sodium was estimated by using linear sweep voltamograms (LSV) on the Na/Na3VS4/Pt and Na/Na3P0.1V0.9S4/Pt cells, as shown in Fig. 5c. Both of LSV curves do not appear apparent redox peak, indicating Na3VS4 and Na3P0.1V0.9S4 solid-state electrolytes exhibit a high electrochemical stability window up to 6 V.

**Conclusion**

In summary, a new Na-ion solid-state electrolyte Na3VS4 with the space group P421c was synthesized and investigated. Na1, Na2, Na3 and Na4 atoms locate at the 4d, 4c, 8e and 8e Wyckoff sites in the structure, respectively. Na2 atom sites bound to eight sulfur atoms and from a body-centered cubic anion framework, which is beneficial for Na ion diffusion. The total ionic conductivity of the parent composition Na3VS4 is ~1.16 × 10⁻⁸ to 1.46 × 10⁻⁶ S cm⁻¹ from 25 to 100 °C. After substituting for V with P, the P-doping composition Na3P0.1V0.9S4, got the conductivity of 1.49 × 10⁻⁷ to 1.20 × 10⁻⁵ S cm⁻¹ from 25 to 100 °C, which was higher than that of parent Na3VS4. The improvement of ion conductivity could ascribe to small P substitution for the large V giving rise to broaden the Na migration path and create of sodium vacancies. Also, both of Na3VS4 and Na3P0.1V0.9S4 solid-state electrolytes exhibit a high electrochemical stability window up to 6 V. This work will enrich the field of view sulfate-based sodium ion conductors and paves a new way to design new solid-state conductors for the next generation of solid-state Na ion batteries.
Conflicts of interest

There are no conflicts to declare.

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