Research Article

Hunting Sodium Dendrites in NASICON-Based Solid-State Electrolytes

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NASICON- (Na superionic conductor-) based solid-state electrolytes (SSEs) are believed to be attracting candidates for solid-state sodium batteries due to their high ionic conductivity and prospectively reliable stability. However, the poor interface compatibility and the formation of Na dendrites inhibit their practical application. Herein, we directly observed the propagation of Na dendrites through NASICON-based $\text{Na}_{3.1}\text{Zr}_2\text{Si}_{2.1}\text{P}_{0.9}\text{O}_{12}$ SSE for the first time. Moreover, a fluorinated amorphous carbon (FAC) interfacial layer on the ceramic surface was simply developed by in situ carbonization of PVDF to improve the compatibility between Na metal and SSEs. Surprisingly, Na dendrites were effectively suppressed due to the formation of NaF in the interface when molten Na metal contacts with the FAC layer. Benefiting from the optimized interface, both the Na||Na symmetric cells and $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ ||Na solid-state sodium batteries deliver remarkably electrochemical stability. These results offer benign reference to the maturation of NASICON-based solid-state sodium batteries.

1. Introduction

Na-ion batteries (NIBs) have been investigated broadly for the potential application particularly in large-scale electrical energy storage due to the infinite sodium resources and relatively low cost [1–6]. Owing to its low electrochemical potential of -2.71 V (vs. standard hydrogen electrode) and high specific capacity of 1166 mAh g^{-1} , Na metal becomes the most attractive anode for NIBs [4, 5, 7–9]. However, failures arising from the formation of Na dendrites and severe side reactions hinder the extensive application of NIBs adopting a Na metal anode coupled with organic liquid electrolytes [10]. Developing solid-state sodium batteries (SSSBs) is regarded as an effective approach to physically stabilize the

Na anode/solid-state electrolyte (SSE) interface, thus suppressing the Na dendrites and side reactions due to the high mechanical strength and wide electrochemical window of SSEs [11, 12]. Besides, higher safety is expected due to the absence of flammable liquid electrolytes [1, 13–18].

In 1976, Goodenough et al. and Hong reported a NASICON-based SSEs, $\text{Na}_{1+x}\text{Zr}_2\text{P}_{3-x}\text{Si}_x\text{O}_{12}$ ($0 \leq x \leq 3$), which demonstrated a considerable high conductivity relying on the open 3D channels for fast Na^+ transport, regarded as one promising candidate of SSEs for SSSBs [19, 20]. A modeling work by Monroe and Newman predicted that Li dendrite growth through the SSE could be mitigated if the shear modulus of the SSE was about twice that of Li metal [21]. Accordingly, the NASICON-based SSSBs are considered to not

FIGURE 1: Schematic illustrations of the Na dendrite propagation in the unmodified NASICON pellet (a) and suppression in the modified NASICON pellet (b).

suffer from Na dendrites due to the relatively higher shear modulus of NASICON-based SSEs (47.7 GPa) than that of Na metal (3.3 GPa) [8, 22]. Though in principle it should work, Na dendrites still caused a short circuit in NASICON-based SSSBs [23–25]. Therefore, the shear modulus of SSEs may not be an appropriate predictor for dendrite inhibition in NASICON-based SSEs.

To suppress the Na dendrites, several interfacial engineering methods have been developed such as higher uniaxial compression [23], composite anode [24], 3D Na metal anode [26], chemically plating interlayer [26], in situ chemically forming interphase [27], and inserting a solid-state polymer electrolyte interlayer [27]. Despite this, the knowledge about how Na dendrites arise and propagate in NASICON-based SSEs is still lacking, and even the evidence of Na dendrites existing in NASICON-based SSEs has not been disclosed yet. Also, all of the strategies mentioned above focused on improving the wettability between NASICON-based SSEs and Na metal; however, the optimization of solid electrolyte interphase (SEI) has been ignored to a certain extent, which is also momentous for stable operation of SSSBs. On the contrary, observations towards Na dendrites have been carried out widely in liquid sodium batteries [10, 28–30]. Therefore, it is urgent to directly observe Na dendrites in SSEs and study the formation and propagation mechanism, based on developing effective strategies to suppress the occurrence of Na dendrites to promote the application of NASICON-based SSEs in SSSBs.

In this study, for the first time, we directly observed the propagation of Na dendrites through polycrystalline

$\text{Na}_{3.1}\text{Zr}_2\text{Si}_{2.1}\text{P}_{0.9}\text{O}_{12}$ (NZSP) SSEs. Furthermore, a fluorinated amorphous carbon (FAC) layer on the NASICON-based SSE surface was developed to improve the wettability between NZSP SSEs and Na metal anode. Meanwhile, this constructed FAC layer was reacted with molten Na metal by simply contacting each other to in situ form a thin SEI composed of NaF, which effectively suppresses the formation of Na dendrites. Benefiting from the FAC-regulated NZSP SSEs, extremely stable Na plating/stripping cycling performance at different current densities on the Na|FAC|NASICON|FAC|Na symmetric cells is demonstrated, and Na dendrites are significantly hindered. The schematic illustrations of the Na dendrite propagation in the unmodified NASICON pellet and suppression in the modified NASICON pellet are shown in Figure 1. Moreover, by further modification of a cathode with PEO-based solid-state polymer electrolyte (PSPE), solid-state sodium battery (SSSB) $\text{Na}_3\text{V}_2(\text{PO}_4)_3|\text{PSPE}|\text{NZSP}|\text{FAC}|\text{Na}$ delivered a stable cycling performance with 96.4% capacity retention after 100 cycles at 1C at 75°C. Our results suggest a feasible strategy for the future development of NASICON-based SSEs in SSSBs.

2. Materials and Methods

2.1. Preparation of NASICON Ceramic Pellets. Nominal composition $\text{Na}_{3.1}\text{Zr}_2\text{Si}_{2.1}\text{P}_{0.9}\text{O}_{12}$ (NZSP) SSEs were synthesized and sintered into ceramic pellets with the traditional ceramic method as reported before [31]. In a typical preparation, under a stoichiometric ratio, Na_2CO_3 , ZrO_2 , SiO_2 and

$\text{NH}_4\text{H}_2\text{PO}_4$ were ball-milled in a planetary ball mill (PM 400, Retsch) at 400 rpm for 12 h. As-obtained mixture was sintered at 1000°C for 10 h in air. The as-sintered product was further ball-milled under the same conditions as described above. The obtained powder was pressed into pellets with 15 mm in diameter and followed by a final sintering process at 1200°C for 20 h where the pellets were covered with mother powder.

2.2. Interfacial Layer for the Anode. 50 mg mL⁻¹ PVDF in NMP solution was spread on the polished NZSP pellets with 10 $\mu\text{L cm}^{-2}$. After evaporating the NMP solvent, the PVDF-coated NZSP pellets were transferred into a tube furnace and sintered at 400°C for 2 h in Ar. Then, the NZSP pellets modified with fluorinated amorphous carbon (FAC) were obtained.

2.3. Material Characterization. X-ray powder diffraction (XRD) was carried out on a D8 advanced X-ray diffractometer (Bruker, Germany) using Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$). Atomic force microscopy (AFM) was conducted on a Multi-Mode 8 SPM (Bruker, Germany). Electrochemical impedance spectroscopy (EIS) was performed by using the IM6e electrochemical workstation with the frequency range from 1 MHz to 100 mHz and an alternating current amplitude of 5 mV (Zahner, Germany). Scanning electron microscopy (SEM) images were obtained on a Hitachi S-4800 in combination with energy-dispersive X-ray spectroscopy (EDX) mapping (Hitachi, Japan). The operando optical microanalysis is conducted on a digital microscope with AM7515 (Dino-Lite, China). X-ray photoelectron spectroscopy (XPS) was conducted using Thermo Scientific ESCLAB 250Xi (Thermo Fisher Scientific, America) equipped with monochromic Al K α radiation, and all spectra were calibrated for the charging effect with the C1s peak at 284.8 eV. Transmission electron microscopy (TEM) was conducted on a JEM-2100Plus (JEOL, Japan). Thermogravimetric analysis (TGA) was conducted on a Diamond TG thermal analyzer (PerkinElmer, America).

2.4. Electrochemical Measurements. The ionic conductivity test was carried out by sputtering a gold film on both sides of the NZSP pellet as ion-blocking electrodes. To evaluate the electrochemical stability of NZSP pellets towards the Na metal anode, the unmodified Na|NZSP|Na symmetric cell was assembled by pressing two pieces of Na metal on two sides of the NZSP pellet. And the interface-modified Na|FAC|NZSP|FAC|Na symmetric cell was prepared by dropping molten Na metal onto the surface of the FAC-modified NZSP pellet. All cells were assembled in a glove box under Ar. The prototype Na|NZSP|Na symmetric cell for operando optical microanalysis is shown in Supplementary Figure S4(o). $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (NVP) was prepared via a one-step ceramic process according to our previous report [3, 32]. And the NVP cathode sheets were prepared by mixing NVP, Super P, PEO, and NaAlg in a mass ratio of 70:15:10:5 in appropriate distilled water to make a homogeneous slurry and spread on an Al foil, which subsequently was dried at 55°C under a high vacuum for

24 h. The average mass loading of the NVP active material is about 3 mg cm⁻². The solid-state polymer electrolyte of PEO-NaFSI (EO/Na⁺ = 15, by molar ratio) (PSPE) was synthesized by a facile solution casting technique according to our previous report [3, 33]. To assemble solid-state batteries, the PSPE interfacial layer was put between NVP and NZSP to improve wettability, so a NVP|PSPE|NZSP|FAC|Na solid-state sodium battery was prepared. All cells were assembled in a glove box under Ar. All the galvanostatic measurements of solid-state batteries assembled in Swagelok cells were conducted on a Land BT2000 battery test system (LANHE, China).

3. Results and Discussion

NASICON-based $\text{Na}_{3.1}\text{Zr}_2\text{Si}_{2.1}\text{P}_{0.9}\text{O}_{12}$ (NZSP) was synthesized and used in this study for the fabrication of SSSBs. The XRD pattern of the as-synthesized NZSP pellet matches the structure of monoclinic C2/c NASICON, as confirmed by the standard diffraction peaks located at around 19.2° and 27.5° (Supplementary Figure S1(a)). Meanwhile, little ZrO_2 impurity appears, which is common during the synthesis of NASICON-based SSEs using a ceramic method [34, 35]. The AFM image of the NZSP surface reveals a polycrystalline structure and dense morphology (Supplementary Figure S1(b)). The resistance of NZSP (thickness of 1.2 mm and diameter of 11.2 mm) was measured by EIS at temperatures from 15°C to 75°C. The conductivities were calculated and fitted well with the Arrhenius equation to demonstrate a good linear relationship with an activation energy of 0.33 eV (Supplementary Figure S1(c)). The Nyquist plots at 25°C and 75°C are shown in Supplementary Figure S1(d), and high conductivities of 1.04 mS cm⁻¹ at 25°C and 5.84 mS cm⁻¹ at 75°C are achieved.

For SSSBs, besides the high ionic conductivity of SSEs, the intimate contact with electrodes to enable a stable and compatible electrode|SSE interface for sufficient ion conduction is the key to improve the electrochemical performances of SSSBs. When the untreated NZSP pellets are employed, the pressed Na metal may not wet the ceramic, forming an inhomogeneous and incompatible interface with many voids and roughness as shown in Figure 1(a) [24, 26]. As a result, the Na⁺ preferentially plates on these voids, roughness, and grain boundaries, where the electric field is locally enhanced, leading to the nucleation and propagation of Na dendrites during Na plating/stripping cycling [27]. Furthermore, Na dendrites can penetrate the interconnected grain boundaries of ceramic and cause a short circuit. To quantitatively evaluate the effect of the untreated NZSP|Na interface, the Na|NZSP|Na symmetric cells were assembled and measured by EIS to obtain the interfacial resistance. The Nyquist plot at 75°C (Supplementary Figure S2) presents a semicircle at medium frequencies associated with the interface response [36]. The interfacial resistance of about 100 Ω is reached, which possibly results from the existing voids and roughness in the interface. After that, the symmetric cell was cycled by periodically charging and discharging, respectively, for 1 h to evaluate the interfacial stability and

FIGURE 2: (a) Galvanostatic cycling of the Na|NASICON|Na symmetric cell at different current densities at 75°C. (b, c) Web-structured dendrite and (d) corresponding EDX mapping. Operando optical observations of Na dendrite propagation in NASICON under (e) 10 μ A, (f) 70 μ A, and (g) 130 μ A for a 2-minute charging process and 2-minute discharging process within the identical cell at prolonged cycling times.

detect whether Na dendrites are formed during this process. As shown in Figure 2(a), ohmic behavior is observed at low current densities less than 0.3 mA cm⁻². It is worth noting that the profiles of charging and discharging processes are getting noisier with increasing current density and capacity; besides, the overpotential of the discharging process is less stable than that of the charging process because of asymmetrical volume changes of the cathode and anode [37]. At 0.3 mA cm⁻², the symmetric cell undergoes an abrupt voltage drop after polarization for a short period,

which may be induced by Na dendrite formation, resulting in the occurrence of the short circuit. Na metal is subjected to 100% volumetric expansion/contraction upon repeated cycling due to its hostless nature [4]. Usually, the plating/stripping of Na metal happens on the interface between SSEs and Na metal, preferentially at the local area but not the whole interface; as a consequence, locally intensified current density near the voids, roughness, grain boundaries, etc. exacerbates the Na dendrite formation during heterogeneous plating/stripping. Besides, it is

reported that NASICON-based SSEs are not stable towards Na metal, and some side reactions have been observed even at room temperature, which partially expedites Na dendrite formation [23, 38].

To examine the reasons for the short circuit, the symmetric cell was disassembled and a clear dark line is observed on the surface of cycled NZSP pellets as shown in the optical photograph of Supplementary Figure S3. Then, we broke the pellet along the dark line for the SEM analysis. The characteristic region of the fracture was detected with a web-like morphology (Figures 2(b) and 2(c)). To further analyze the composition of the detected regions, EDX mapping was conducted and composed of Na element (Figure 2(d)). It is interesting to note that the web-like morphology is very similar to that of the intergranular Li dendrites observed in garnet SSEs as reported by Cheng et al. [39]. Therefore, Na dendrites are confirmed according to the above analysis, which is visually observed in the NZSP electrolyte for the first time to the best of our knowledge. According to previous investigations, we believe that the inhomogeneous current distribution induced by the nonuniform interfacial connection between Na metal and SSEs, the infinite volume change of Na metal, and the unreliable SEI are the key to cause Na dendrite formation, thus inducing the short circuit. Besides, due to the polycrystal essence and the different Na^+ conductivities in grain and grain boundary of NASICON, the Na metal would propagate along the NASICON grain boundaries to form a web [39]. Furthermore, for observing the Na dendrite propagation in the NASICON pellet more intuitively, operando optical microanalysis was conducted. Figures 2(e)–2(g) show optical images of Na dendrites after 2-minute charging and 2-minute discharging processes at $10\ \mu\text{A}$, $70\ \mu\text{A}$, and $130\ \mu\text{A}$, respectively. And more images under different current are provided in Supplementary Figure S4; meanwhile, the movie of the operando optical microanalysis is provided in Supplementary Movie S1. From which, it can be seen that Na dendrites preferentially germinate on the tips where the electric field is locally enhanced as circled in Figure 2(e). Besides, with increasing current density, the Na dendrites gradually propagate towards the counter electrode and get short circuit at $130\ \mu\text{A}$ as circled in Figure 2(g). More seriously, once the Na dendrites are formed, they do not disappear but continue to grow on the original basis until getting short circuit. Hence, it is urgent to realize the dendrite-free NASICON-based SSEs by interfacial modification.

Carbonaceous materials, regarded as excellent interface layers and/or host frames for metal electrodes due to their high electronic conductivity and flexible nature, have been widely employed as modifying material in liquid- and solid-state batteries [40–44]. Besides, it is believed that the presence of NaF in SEI is effective by its stabilizing effect on the Na metal surface for enabling dendrite-free, uniform, and dense Na plating [8, 45, 46]. Therefore, if a carbon interface layer can be constructed between the Na metal anode and NZSP SSE with an in situ-formed SEI containing NaF, SSSBs are expected to deliver a splendid performance. Inspired by this idea, we chose PVDF with a high content of both C

and F elements to build the interface layer. PVDF can be carbonized at low temperatures in Ar as confirmed by TGA as presented in Supplementary Figure S5(a). The in situ carbonization of PVDF on the surface of the NZSP pellet was realized as shown in Figure 3(a), where the inset map confirms the amorphous nature of PVDF-derived carbon. The lateral digital photo in Figure 3(b) demonstrates the excellent wetting of FAC-modified NZSP towards Na metal, and the top view is shown in Supplementary Figure S5(b). Furthermore, the SEM image in Figure 3(c) confirms the close connection between Na metal and FAC-modified NZSP pellets, where the sodiated FAC layer modifies the uneven surface of the NZSP pellet effectively. EDX mapping further reveals that the FAC layer can effectively improve the wetting property of NZSP SSEs with Na metal as shown in Figures 3(d)–3(f).

The XPS spectra shown in Figures 3(g) and 3(h) are the C1s, F1s, and Na1s spectra of the FAC layer before (Figure 3(g)) and after (Figure 3(h)) contacting with molten Na. The fitted XPS spectra of C1s and F1s in the original FAC layer indicate that the F element exists in C-F bonds as shown in Figure 3(g), which further suggests the fluorinated amorphous carbon nature of the PVDF-derived interfacial layer. As expected, the Na element from NZSP is not detected due to the fact that the thickness of FAC exceeds the detecting depth of XPS. After reaction with molten Na metal, C1s and F1s in FAC remarkably changed as presented in Figure 3(h). The C1s peaks of F-C-* and F-C* disappear, and the F1s peak shifts towards lower binding energy, suggesting the breaking of C-F bonds and generation of Na-F bonds. Besides, the fitted XPS spectrum of Na1s further confirms the reaction between molten Na metal and the FAC layer with the formation of NaF.

According to the above results, the interphase composed of the carbonaceous material and NaF inorganic salt was successively in situ formed as our original design. To verify the effect of FAC modification on the improvement of the Na|NZSP interface, EIS was used to quantify the change of the interfacial resistance. One half of the decrease is observed in Supplementary Figure S2(b) compared with original interfacial resistance as shown in Supplementary Figure S2(a). The decreased resistance can be attributed to the better connection between Na metal and NZSP pellets due to the modification of the FAC layer, which alleviates surface voids and roughness and provides superior wetting behavior. Galvanostatic cycling experiments are carried out to evaluate the capability of suppressing Na dendrites and the diffusion of Na^+ across the interface as shown in Figure 4. At $0.1\ \text{mA cm}^{-2}$ current density, the Na|FAC|NZSP|FAC|Na cell stabilizes at around 6 mV, and stable cycling below $0.6\ \text{mA cm}^{-2}$ is reached, well according to the ohmic behavior. It is worth noting that the polarization voltages of charging and discharging processes get more stable than those of the symmetric cell based on the untreated NZSP. The asymmetrical effect of volume changes at the cathode and anode has been suppressed benefitting from the flexible nature of the FAC layer and the homogeneous Na^+ flux across the interface. More importantly, there is no abrupt

FIGURE 3: FAC-treated NZSP. (a) Digital photo of the PVDF-derived layer on the surface of NZSP. Inset is the XRD profile of PVDF-derived carbon. (b) Optical photograph of melted Na metal on top of the NZSP pellet. (c) SEM image of the FAC-treated NZSP pellet. EDX mapping of (d)–(f) revealing the distribution of F, Na, and P elements near the interface between Na metal and NZSP pellet. C1s, F1s, and Na1s XPS spectra from (g) untreated and (h) FAC-treated NZSP pellets.

drop in the overpotential when polarization is at 0.6 mA cm^{-2} ; inversely, an abrupt open circuit is observed for a period. This phenomenon confirms the excellent capability of the FAC layer to suppress Na dendrites. All the results suggest that the FAC layer realizes the excellent interfacial contact, facilitates the Na^+ diffusion across the interface, improves the interfacial stability, and especially possesses a superior capability of suppressing Na dendrites.

To evaluate the electrochemical performance of FAC-modified NZSP, SSSBs were assembled with NVP as a cathode, Na metal as an anode, and FAC-modified NZSP as the electrolyte. The synthesized NVP cathode delivers a pure rhombohedral R-3c structure as confirmed by XRD (Supplementary Figure S6(a)). The SEM image (Supplementary Figure S6(b)) confirms the uniformly distributed nanoparticles. The HRTEM image (Supplementary

FIGURE 4: Galvanostatic cycling of the Na|NASICON|Na symmetric cell at different current densities at 75°C.

FIGURE 5: NVP|PSPE|NZSP|FAC|Na ASSSB at 75°C: (a) the galvanostatic charge and discharge profile at 1C; (b) cycling performance at 1C (0.3 mA cm^{-2}).

Figure S6(c)) shows a homogenous 4 nm carbon coating layer on the NVP particle and the corresponding lattice fingers of (104) and (102) planes of NVP. Supplementary Figure S6(d) shows the SEAD image corresponding to the area shown in Supplementary Figure S6(c), which further confirms the rhombohedral structure of the as-synthesized NVP. Besides, to wet the interface between NVP and NZSP, PEO-NaFSI PSPE was prepared and inserted. And the good compatibility between NVP and PSPE has been illustrated elsewhere [33, 47]. The Arrhenius plot of Na^+ conductivity of PSPE is shown in Supplementary Figure S7(a), and high ionic conductivity of 0.432 mS cm^{-1} at 75°C is reached. Moreover, as presented in Supplementary Figure S7(b), the high thermal decomposition temperature of around 240°C ensures the high safety of ASSSBs. A high initial discharge

capacity of 95.2 mAh g^{-1} and 97.84% Coulombic efficiency at 1C were achieved for NVP|PSPE|NZSP|FAC|Na ASSSB as shown in Figure 5(a), before which a low current density of 0.1C was applied to aim at electrochemically forming interphases for both the cathode and anode. Supplementary Figure S8 shows the first 3 cycles of charging and discharging profiles at 0.1C. After 100 cycles at 1C, the ASSSB demonstrates 96.4% capacity retention with 91.8 mAh g^{-1} and nearly 100% Coulombic efficiency as shown in Figure 5(b). The superior cycling stability could be attributed to the excellent wettability of PSPE towards the NZSP and NVP cathode, and more importantly, that the FAC interfacial layer provides the splendid interface reliability between NZSP and Na metal anodes, ensuring interfacial contact and suppressing Na dendrites. Besides,

the NaF in the interfacial layer also contributes to enabling uniform and dense Na plating.

4. Conclusion

In summary, we presented direct evidence for the first time that Na dendrites can propagate through the hard NASICON ceramic, which is crucial for understanding the mechanism of occurrence and propagation of Na dendrites in NASICON-based solid-state electrolytes. Furthermore, we developed a FAC layer on the NASICON ceramic pellet surface by in situ carbonization of PVDF to improve the wettability between Na metal and NASICON, where NaF was in situ formed in the SEI to enhance the interfacial stability. Benefiting from the optimized interphase, the Na||Na symmetric cell shows much better cycling stability, significantly inhibiting the sodium dendrites. Combined with the PSPE cathode interlayer, the fabricated NVP|PSPE|NZSP|FAC|Na SSSBs delivered excellent electrochemical stability, demonstrating 96.4% capacity retention at 1C after 100 cycles. The results in this study are expected to provide a feasible strategy for the research and application of NASICON-based SSEs in SSSBs.

Data Availability

The authors declare that the main data supporting the findings in this study are available within the article and its supplementary information. Additional data are available from the corresponding authors upon reasonable request.

Conflicts of Interest

The authors declare no competing interests.

Authors' Contributions

Y.X.L., Y-S.H., X.G.H., H.L., and L.Q.C. proposed and designed the project. Q.Q.Z. synthesized the electrolyte and electrode materials and performed electrochemical measurements and carried out characterizations. W.C.G. performed the operando optical microanalysis. Y.J.S. and L.L.L. performed the XPS analysis. J.Z.L. carried out the AFM characterization. X.H.R. drew the schematic diagram of Figure 1. Q.Q.Z., Y.X.L., Y-S.H., and X.G.H. wrote the manuscript. All authors discussed the results and commented on the manuscript.

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Supplementary Materials

Supplementary 1. Figure S1: $\text{Na}_{3.1}\text{Zr}_2\text{Si}_{2.1}\text{P}_{0.9}\text{O}_{12}$. (a) XRD patterns (C2/c, COD: 1529608; R-3c, COD: 1529809). (b) AFM morphology of the surface. (c) Arrhenius plot of total conductivity vs. reciprocal temperature. (d) Nyquist plot at 25°C and 75°C. Figure S2: Na||Na symmetric cell. (a) EIS profile for the Na|NZSP|Na symmetric cell at 75°C. (b) EIS profile for the Na|FAC|NZSP|FAC|Na symmetric cell at 75°C. Figure S3: optical photograph of the short-circuited NZSP. Figure S4: operando optical observations of Na dendrite propagation in NASICON under different current for a 2-minute charging process and 2-minute discharging process. (a) Origin. (b) 10 μA . (c) 20 μA . (d) 30 μA . (e) 40 μA . (f) 50 μA . (g) 60 μA . (h) 70 μA . (i) 80 μA . (j) 90 μA . (k) 100 μA . (l) 110 μA . (m) 120 μA . (n) 130 μA . (o) Optical photograph of the Na||Na symmetric cell after cycling. Figure S5: (a) TGA trace of PVDF from 50°C to 800°C. (b) Digital photo of molten Na metal on top of the NZSP surface. Figure S6: $\text{Na}_3\text{V}_2(\text{PO}_4)_3$. (a) XRD pattern. (b) SEM image. (c) HRTEM image. (d) Corresponding SEAD pattern. Figure S7: PEO15-NaFSI. (a) Ionic conductivity at different temperatures. (b) TGA trace from 50°C to 650°C. Figure S8: the galvanostatic charge and discharge profile for the first 3 cycles of NVP|PSPE|NZSP|FAC|Na AASSB at 0.1C and 75°C. The low Coulombic efficiencies in first 3 cycles (84.37%, 93.13, and 94.8%) contributed to the formations of SEI at the anode and CEI at the cathode.

Supplementary 2. Movie S1: the movie of the operando optical microanalysis.

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