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Ultrafast Synthesis of Nasicon Solid Electrolytes for Sodium-Metal Batteries

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NASICON-structured solid-state electrolytes (SSEs) are highly promising materials for sodium solid-state metal batteries (NaSMBs). However, the current synthesis methods are often labor-intensive and inefficient, consuming a significant amount of energy and time. Here, an ultrafast high-temperature synthesis (UHS) technique is successfully demonstrated to directly synthesize NASICON-type SSEs from mixed precursor powders, reducing the synthesis time from hours to merely seconds. The intermediate with a Na₃PO₄ structure plays a critical role in the rapid synthesis of NASICON-type SSEs, ultimately leading to the formation of the final NASICON phase. Moreover, the UHS-synthesizes NASICON-type Na_{3 3}Zr_{1 7}Lu_{0 3}Si₂PO₁₂ (NZLSP) exhibits high room temperature ionic conductivity of 7.7×10^{-4} S cm⁻¹, approximately three times that of the undoped Na₃Zr₂Si₂PO₁₂ (NZSP). The Na|NZLSP|Na symmetric cell can sustain highly stable cycling for over 4800 h. This study provides a novel insight and validation in the precise and targeted synthesis of complex oxide solid-state electrolytes.

1. Introduction

Sodium-ion batteries (SIBs) are regarded as one of the most competitive alternatives to lithium-ion batteries (LIBs) because of

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their low cost and abundant availability of raw materials.^[1-3] Due to its high theoretical specific capacity (1165 mAh g⁻¹) and low redox potential (-2.714 V vs SHE). the utilization of sodium metal as anodes can further boost the energy density of SIBs.^[4–6] However, the highly reactive nature of Na metal and the flammability of organic electrolytes in sodium metal batteries (NaMBs) pose potential safety hazards, which could result in internal short circuits, thermal runaways, and even fires.^[7-9] To overcome these issues, solid-state electrolytes (SSEs) replacing organic electrolyte and separators offer a safer solution as they obtain good stability, non-flammability, environmental friendliness, and do not pose a risk of leakage.[10-15]

Among all types of SSEs, inorganic solid oxide electrolytes have been

reported with attractive advantages such as high ionic conductivity, low electronic conductivity, high mechanical strength, and high Na⁺ transference number.^[16-19] Among them, NASI-CON structure SSEs, first discovered by Goodenough and Hong et al. in 1976,^[20,21] are known for their stability in moist environments, safety, and 3D diffusion pathways, considered ideal sodium ion solid electrolyte materials.^[22-24] The general formula of NASICON-type SSE is $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ($0 \le x \le 3$).^[25] When x = 2, the pristine Na₃Zr₂Si₂PO₁₂ (NZSP) obtains the reportedly highest ionic conductivity, reaching 6.7×10^{-4} S cm⁻¹ at 25 °C and 0.2 S cm $^{-1}$ at 300 °C, respectively. $^{[26-28]}$ To boost the practical application of NASICON type SSEs for NaMBs, a higher ionic conductivity, lower electronic conductivity and interface resistance of NZSP still needs further optimizations. However, due to the limitation of conventional solid-state synthesis methods such as high temperatures (>1000 °C) and long operation hours (>10 h),^[29–31] a high-throughput, fast screening, and precise synthesis of high performance NZSP is yet to be demonstrated, to the best of our knowledge. Moreover, the conventional long-term high-temperature process not only increases the likelihood of undesired secondary phases, but also will lead to the volatilization of Na/P elements, inhibiting the formation of the material in its pure form and limiting its performance.[32-34] Therefore, the rapid synthesis and optimization of high-performance NZSP materials remain a significant challenge. A method that can quickly produce pure materials in a high-throughput manner could greatly enhance the optimization efficiency of NZSP.

A class of ultrafast synthesis methods has attracted tremendous attention recently,[35] among which ultrafast hightemperature sintering (UHS) with joule heating being one of the most promising methods.^[36-38] It has been successfully demonstrated to synthesize various types of materials from nanoscale to bulk form, with specimen production time typically taking only seconds or less.[39-41] Although the UHS method has been successfully used to synthesize garnet-structured Li SSEs,^[42] no reports have been made about UHS synthesis of Na SSEs. Previous effects have only reported rapid sintering, instead of synthesis, of NZSP pellets from pre-synthesized NZSP powders.^[43,44] This is likely due to the complex nature of solid-state synthesis,^[45–47] which involves a multi-step process of mixing, heating, reacting, and annealing the starting materials and the intermediates. In the case of complex oxides such as NZSP, these steps are critical to the formation of final product, yet the reaction pathways and mechanism are not well understood. Due to the intricate nature of solid-state reactions and the ambiguous understanding of the reaction mechanism in NASI-CON materials, the rapid synthesis of pristine NZSP SSEs using UHS technology is unattainable, as clearly demonstrated by our experimental findings in Figure 1b. Consequently, the synthesis of pristine NZSP SSEs can solely be accomplished through conventional furnace-synthesized technology. Hence, the unresolved challenge persists in the preparation of NASICON-type SSEs using the UHS technique.

In this work, we successfully demonstrate the preparation of NASICON-type SSEs using the UHS method through appropriate doping, which the reaction pathway and mechanism is further analyzed. Our findings indicate that only when specific elements like Tm, Yb, and Lu are doped, can the NASICON phase be synthesized through UHS. Our further experimentation and analysis suggest that these selected elements can assist in forming an intermediate phase that catalyzes the formation of the NASICON phase. Compared to conventional synthesis methods, our UHS approach significantly reduces the synthesis time from hours to merely seconds, enabling the product in a pure solid crystalline phase. In addition, our experiments reveal that the room-temperature ionic conductivity of the UHSsynthesized Na33Zr17Lu03Si2PO12 (NZLSP) SSEs is nearly three times higher than that of the furnace-synthesized NZSP SSEs. Notably, the Na|NZLSP|Na symmetric cells demonstrate a critical current density up to 1.4 mA cm⁻² and stable cycling for over 4800 h with a low overpotential of 30 mV at a current density of 0.1 mA cm⁻². This work presents an effective, time- and energysaving pathway for the rapid synthesis of NASICON-type solid electrolytes, opening up avenues in facilitating precise and accelerated discovery of complex functional materials.

2. Results and Discussion

The typical UHS synthesis process is illustrated in Figure 1a. A mixed precursor of Na_2CO_3 , $NH_4H_2PO_4$, ZrO_2 , SiO_2 , and Lu_2O_3 is first pressed under uniaxial pressure into a dense, green pellet, which is then sandwiched between two carbon felts and rapidly heated through joule heating in Ar atmosphere (Figure S1, Supporting Information). The temperature of the carbon felts is calibrated by an infrared camera, which is roughly proportional to the applied current (Figure S2, Supporting Information). As

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shown in Figure 1b, the pristine NZSP cannot be directly synthesized from precursors using UHS. Surprisingly, when the starting precursor is combined with Lu₂O₂, the Lu-doped NZSP at the Zr site can generate the NASICON phase using UHS. To explore the optimized synthesis parameters, we studied the NASICON phase formation of NZLSP SSEs by XRD under different UHS synthesis conditions (Figure S3, Supporting Information). The degree of NASICON phase formation was quantified by the peak intensity ratio (PIR) from the corresponding products' XRD spectrum. The PIR was defined and calculated based on the following equation: $PIR = [I(111)_{II} + I(110)_{II} + I(020)_{II}]/I(111)_F + I(110)_F$ + $I(020)_{F}$, where I represents the intensity of three strongest characteristic peak of NZSP SSE, U and F represents the UHS synthesis process and the furnace synthesis process, respectively. As shown in Figure 1c, the PIR obtained the maximum value (\approx 100%) when the pellet are heated at \approx 1880K for 8s, indicating the UHS-synthesized material can obtain almost the same NASICON phase as the furnace-synthesized material (Figure S4, Supporting Information). Notably, our UHS approach eliminates the presence of undesirable secondary phases, which are often produced in conventional synthesis methods due to prolonged holding and cooling times.^[48-50] This results in improved homogeneity and purity of the final materials.

We further investigated the effect of Lu content on the synthesis of $Na_{3+x}Zr_{2-x}Lu_xSi_2PO_{12}$ ($0 \le x \le 1$) using the UHS method. Our experiments indicate that the material can only form a pure NASICON phase when the Lu doping amount is within a certain range (also see Figure S5, Supporting Information), which highlights the cruciality of Lu content in the NASICON formation. Furthermore, we observed the morphological features of as-obtained NZLSP. As depicted in SEM images of different UHS time (Figure S6, Supporting Information), the precursors of NZLSP quickly react and densify in ≈8s as the heater temperature approaches ≈1880 K. Figure 1d shows that the distinct lattice spacing of 0.32 and 0.46 nm corresponds to the (-222) and (111) plane, respectively, further confirming the formation of the monoclinic NASICON phase. The EDS mapping of NZLSP SSEs shows a homogeneous distribution of Na, Zr, Lu, Si, O, and P elements (Figure 1e; Figure S7, Supporting Information), revealing the accurate and uniform incorporation of the Lu dopants.

We further explored the universality of our UHS strategy in synthesizing the NASICON phase of other single element-doped systems, covering most commonly reported NASICON dopants to the best of our knowledge. These doping elements can be mainly classified into alkaline earth metals, transition metals, and rare earth metals. As shown in Figure 2a, it is evident that most dopants are unable to be doped at the Zr⁴⁺ position through UHS process (Figure S8, Supporting Information), leading to the failure of NASICON phase formation. For example, according to Figure 2b, when the doping elements are Nd, Hf, and Mg, the prominent diffraction peaks of materials after 8 s of UHS treatment correspond to the standard peak of baddelevite-ZrO₂, confirming the failure in these doping elements. Other strategies such as prolonging time and adjusting temperature also fail to synthesize precursors with such dopants in NASICON phase. In contrast, according to Figure 2c, when the doping elements are Lu, Yb, and Tm, the $Na_vZr_{2-x}M_xSi_2PO_{12}$ (M = Lu, Yb, and Tm) SSEs with NASICON phase can be successfully synthesized under the similar UHS conditions.

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Figure 1. Ultrafast synthesis of NASICON-type solid electrolytes. a) Temperature versus time curve and schematics of the ultrafast synthesis process. b) XRD patterns of undoped and Lu doped NZLSP SSEs under different ultrafast synthesis conditions. c) Key parameter (time and temperature) selection of NASICON phase formation for NZLSP SSEs in ultrafast synthesis. d) HRTEM of a NZLSP SSE particle and corresponding e) EDS mappings of O, Zr, P, Na, Lu, and Si elements.

To understand the NASICON phase formation process during UHS treatment, we performed ex situ XRD analysis on the materials with and without Lu dopant. As shown in Figure 2d, at the start of the UHS reaction after ball milling, the dominant phases of the Lu-doped material are Na_3PO_4 , ZrO_2 , and Lu_2O_3 . The diffraction peak of SiO₂ precursor cannot be detected, sug-

gesting it is nearly amorphous (Figure S9, Supporting Information). As the UHS reaction time increased to 5 s, the diffraction peaks of Lu_2O_3 disappear, and the prominent peak of Na_3PO_4 shifts to a lower angle, indicating that the disappeared Lu element may have dissolved into the Na_3PO_4 structure. As the UHS time increased further, the NASICON phase begins to form due



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Figure 2. Ultrafast synthesis of NASICON SSEs with commonly reported single dopants. a) Different elements doped in the Zr⁴⁺ site for NASI-CON SSEs from our experiments. b) XRD patterns of as-synthesized Na_yZr_{2-x}M_xSi₂PO₁₂ (M = Nd, Hf, and Mg). c) XRD patterns of as-synthesized Na_yZr_{2-x}M_xSi₂PO₁₂ (M = Lu, Yb, and Tm). d) Ex situ XRD measurements captured during the synthesis of NZLSP at 1880K at different synthesis time period.

to the reaction between the solid solution Na_3PO_4 intermediate phase (NLSP) and ZrO_2 . Finally, when the UHS time increased to 8 s, the pure NASICON phase can be formed. Conversely, for the undoped group, NZSP phase is difficult to synthesize directly from the precursor using the UHS method, the prominent peaks are only ZrO_2 and Na_3PO_4 throughout the entire UHS process (Figure S10, Supporting Information). This suggests that the Na_3PO_4 intermediate phase without Lu dopant is not favorable in forming NASICON phase during the UHS synthesis process. Therefore, the NLSP intermediate phase plays a vital role in the formation of the NASICON phase, which can promote the successful synthesis of SSEs with NASICON structure.

To validate our hypothesis on the reaction pathway for UHS of NASICON, we further synthesized the NLSP intermediate phase using the UHS method, as depicted in **Figure 3a**. We first selected raw materials as Na₂CO₃, NH₄H₂PO₄, SiO₂, and Lu₂O₃ to form the NLSP intermediate phase. We utilize the temperature to prepare NLSP similar to that of the NASICON phase formation, which is ≈1880K. As the reaction time increases, we observed the vanishing of Lu₂O₃ peak and the blue shift of Na₃PO₄ peak, indicating that the Lu element gradually dissolves into the Na₃PO₄ structure (Figure S11, Supporting Information). After 5 s of reaction, the NLSP intermediate phase with a Na₃PO₄ structure is formed (Figure 3b). We also observed that SiO₂ may play a critical role in forming the Lu-Na₃PO₄ intermediate, as the Lu₂O₃ peak still exist in mixed powder (starting with ball milled Na₂CO₃,

NH₄H₂PO₄, and Lu₂O₃ but without SiO₂) after UHS regardless of treatment time (Figures S12 and S13, Supporting Information). The phase structure of the NLSP intermediate phase is further revealed through TEM characterization. In Figure 3c,d, the local high-resolution morphology shows a 0.18 nm lattice spacing corresponding to the (400) plane, indicating the formation of the Na₃PO₄ phase. Moreover, the EDS mapping in Figure 3e exhibits the uniform distributions of Si, P, O, Na, and Lu elements in the NLSP intermediate phase. The incorporation of Lu may activate the structure of Na₃PO₄, which may promote the phase transformation reaction between the NLSP intermediate phase and ZrO₂ during the UHS process. To demonstrate that the intermediate phase is a critical step toward the rapid synthesis of the NASICON phase, we conducted UHS experiments using NLSP and ZrO₂ as raw materials and successfully synthesized the NASICON phase (Figure 3f). The obtained material based on NLSP intermediate phase exhibits a strong diffraction peak corresponding to the monoclinic NASICON phase (No. 84-1200) in Figure 3g. The lattice spacing observed in Figure 3h,i corresponds to the (-111) crystal plane, consistent with the XRD results. The high crystal integrity of the NASICON SSEs is confirmed through EDS mapping, which shows uniform distributions of Na, Zr, Lu, Si, O, and P elements (Figure 3j; Figure S14, Supporting Information). This intermediate assistant synthesis approach reduces the number of precursors, thereby limiting the possible number of reaction pathways in the synthesis process.

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Figure 3. Synthesis of the NASICON phase based on the NLSP intermediate phase. a) Schematic diagram of NLSP synthesis process. b) XRD patterns of NLSP intermediate phase. c) TEM and d) HRTEM of NLSP intermediate phase. e) EDS mappings of Si, P, O, Na, and Lu elements for NLSP. f) Schematic diagram of NASICON phase synthesis process based on NLSP intermediate phase. g) XRD patterns of NASICON-type NZLSP SSEs synthesized with NLSP intermediate and ZrO₂. h) TEM and i) HRTEM of NASICON-type NZLSP SSEs. j) EDS mappings of Lu, O, P, Na, Si, and Zr elements for NASICON-type NZLSP SSEs.

This leads to greater simplicity and controllability in the synthesis of complex oxide materials.

The ionic conducting properties of UHS-assisted NASICONtype NZLSP SSEs were measured using electrochemical impedance spectroscopy (EIS). As shown in **Figure 4**a, the room-temperature impedance of NZLSP is significantly lower than that of undoped NZSP. The ionic conductivity of NZLSP SSEs was calculated to be up to 7.7×10^{-4} S cm⁻¹, which is approximately three times higher than that of undoped NZSP (2.8×10^{-4} S cm⁻¹). Furthermore, as shown in Figure 4b, the Arrhenius plots indicate that the activation energy of NZLSP SSEs is 0.30 eV, lower than that of NZSP SSEs (0.36 eV). That is, Lu³⁺ substitution can effectively reduce the activation energy of pristine NZSP SSEs, thereby improving the transport of Na⁺ ions and the higher ionic conductivity. The XRD patterns with Rietveld refinements of NZSP and NZLSP, as depicted in Figure 4c,d, confirm the successful substitution of Zr⁴⁺ with Lu³⁺. The Na-ion diffusion pathways in the monoclinic NZSP were determined by the BVSE method. As shown in Figure 4e, the Na1 sites are connected through the Na1-Na2-Na1 and Na1-Na3-Na1 channels. From the previous studies,^[51,52] the bottleneck B (or B') in the Na1-Na2-Na1 channel (Figure 4f) is the limiting factor for Na⁺ ion conduction. The bottleneck sizes based on the XRD data (Tables S1 and S2, Supporting Information) were assessed with the utilization of the radii of the circumcircles of the corresponding bottleneck triangles whose vertices are the O²⁻ ions.^[29,52,53] When the migrating Na⁺ ion is passing though the bottleneck triangles (Figure S15, Supporting Information), the Na⁺ ion and the O²⁻ ions are three coordinated. Thus, the suitable size of the bottleneck is ≈ 2.35 Å which equals the oxygen radius (1.36 Å) plus the sodium radius (<0.99 Å) according to the Shannon effective ionic radii table.^[54]

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Figure 4. The ionic conducting properties of NASICON-type SSEs. a) Room-temperature EIS plots of NZSP and NZLSP SSEs. b) Arrhenius plots of NZSP and NZLSP SSEs. c) Room temperature XRD patterns with Rietveld refinements results of NZSP. d) Room temperature XRD patterns with Rietveld refinements results of NZSP. d) Room temperature XRD patterns with Rietveld refinements results of NZSP. d) Room temperature XRD patterns with Rietveld refinements results of NZSP. d) Room temperature XRD patterns with Rietveld refinements results of NZLSP. e) BVEL maps of NZSP system with isosurfaces drawn at the 1.6 eV level above E_{min} . f) Location of bottlenecks A, B, B', and A' in Na1–Na2–Na1 channel. g) Comparisons of size of different bottlenecks in Na1–Na2–Na1 channel for NZSP and NZLSP system.

Figure 4g demonstrated that the substitution of Zr⁴⁺ by Lu³⁺ tailors the sizes of the bottlenecks A from 2.439 to 2.430 Å and the bottlenecks B from 2.156 to 2.188 Å which are more closer to the ideal size (2.35 Å). In addition, as our previous work suggested,^[55,56] the increased Na⁺ concentration (due to Lu doping) can promote the correlated jumps with low migration barrier and correspondingly enhance the Na-ion conductivity. Therefore, compared to the pristine system, the Lu-doped NZSP has the optimal bottleneck sizes and the increased Na⁺ concentration, which lead to higher Na⁺ conductivity.

To evaluate the electrochemical performance of the UHSsynthesized NZLSP, we investigate its electrochemical performance. **Figure 5**a shows the direct current (DC) polarization curves of NASICON SSEs. The electronic conductivity of the NZLSP sample is calculated to be as low as 6.6×10^{-9} S cm⁻¹ at room temperature, significantly lower than the undoped NZSP sample, 1.1×10^{-8} S cm⁻¹ under the same conditions. Figure 5b illustrates Nyquist plots of the NASICON electrolyte-based symmetric cell, where the intercept on the real axis represents the bulk resistance of the electrolyte. The semicircle is assigned to the interfacial resistance between the Na metals and the electrolyte, as well as the grain boundary resistance of the electrolyte.^[57–59] By substituting Zr⁴⁺ with Lu³⁺, the total resistance is significantly reduced to about 600 ohms, whereas the pristine NZSP electrolyte cell has a resistance of nearly 1800 Ω . This indicates that Lu doping can also enhance the affinity between Na and NASICON-type SSEs, thus significantly reducing the interface resistance.

To investigate the Na dendrite suppression capability of the NASICON electrolytes, Na|NASICON|Na symmetric batteries were tested at room temperature. Figures 5c,d show the results of the galvanostatic charge/discharge cycling tests conducted at different current densities from 0.1 to 1.5 mA cm⁻² with a step increase of 0.1 mA cm⁻². As shown in Figure 5d, no short circuit occurred when the current density increased to 1.4 mA cm⁻² for Na|NZLSP|Na symmetric battery. However, for the Na|NZSP|Na symmetric battery, a short circuit occurred due to dendrite penetration when the current density surpassed 0.6 mA cm⁻², as shown in Figure 5c. This result indicates that Lu doping can significantly improve the critical current density (CCD) of NASICON electrolytes. We investigated the stability of the NASICON electrolyte against Na metal using a symmetrical Na|NASICON|Na cell at a current density of 0.1 mA cm⁻² under room temperature. As presented in Figure 5e, the potential polarization in symmetrical Na|NZSP|Na cell gradually increased during the initial Na plating/stripping and then stabilized after 1500 h. Conversely, the overpotential upon long-term cycling in Na|NZLSP|Na symmetrical cell did not increase, and

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Figure 5. The electrochemical performances of NASICON-type SSEs. a) DC polarization curves of NZSP and NZLSP samples. b) Nyquist plots of Na metal symmetric cells based on NZSP and NZLSP SSEs. Galvanostatic cycling of Na|NASICON|Na symmetric battery with c) NZSP and d) NZLSP SSEs at step-increased current density. e) Prolonged galvanostatic cycling of Na|NASICON|Na symmetric battery with NZSP and NZLSP SSEs at a current density of 0.1 mA cm⁻².

the symmetric battery remained stable, cycling over 4800 h at 0.1 mA cm^{-2} without any dendrite penetration.

We conducted further experiments to investigate the different behavior of NASICON SSEs before and after Lu doping in symmetrical cells. First, the contact state between Na metal anodes and NASICON SSEs pellets was examined. Figure S16 (Supporting Information) shows that the Lu-doped NZSP pellet exhibited comparably better wettability to the pristine NZSP, indicating a reduction in surface tension between the NASICON SSEs and molten Na metal anodes. Consequently, the non-tight interfacial connection between Na metal and SSEs, leading to an inhomogeneous current distribution, was identified as a factor causing higher polarization. Second, a detailed analysis of the morphology of the surface and cross-section of the cycled pellets was performed. As depicted in Figure S17a and b (Supporting Information), the surface of cycled NZSP SSEs displayed uneven sodium deposition relative to that of cycled NZLSP SSEs. Additionally, a significant number of voids were observed on the cross-section of NZSP SSEs (Figure S18, Supporting Information), resulting in a higher likelihood of sodium dendrite formation during cycling (Figures S17c,d, and S19, Supporting Information), which corroborates the findings of Hu et al. [60] These results support the

notion that the locally intensified current density near the voids exacerbates the formation of Na dendrites during heterogeneous plating/stripping, thereby contributing to increased polarization and lower CCD in undoped samples.

Besides, we assembled and tested the performance of solidstate sodium batteries based on as-synthesized NASICON SSEs, with Na₃V₂(PO₄)₃ (NVP) as cathode and Na metal as anode. As shown in Figure S20 (Supporting Information), the NASICON SSEs, both before and after Lu doping, exhibits a capacity retention rate of over 95% after 30 cycles at 0.1 C. Compared to undoped NZSP SSEs, the Lu-doped NZSP SSEs demonstrate higher discharge specific capacity (84 mAh g⁻¹) and Coulombic efficiency (>99%), further validate its better performance for solidstate sodium batteries. The high ionic conductivity, low electronic conductivity, high CCD, and excellent Na plating/stripping stability make NZLSP SSEs a promising candidate for application in all-solid-state sodium batteries.

3. Conclusion

In summary, we successfully demonstrate the use of UHS technique to directly synthesize sodium-ion conductors with the NA- SICON structure from mixed pristine precursor powders. Compared to traditional solid-state synthesis methods, our approach significantly reduces the synthesis time of NASICON-type solid electrolyte from hours to just seconds, resulting in a pure NASI-CON phase sample. Our findings indicate that the synthesis of the NASICON phase with the formula of $Na_{3+x}Zr_{2-x}M_xSi_2PO_{12}$ (M = Tm, Yb, Lu, $x = 0.3 \sim 0.7$) through UHS is only achievable when certain elements like Tm, Yb, and Lu are doped, whereas for common dopants such as Mg, Zn, Y, Hf, and La, the NASI-CON phase cannot be generated using UHS. Our further experimentation and analysis suggest that the selected dopants such as Lu can form a NLSP intermediate phase that catalyzes the formation of the NASICON phase. This intermediate phase may reduce the energy barrier of the entire solid-state reaction and ensure uniform diffusion of elements during rapid synthesis, which is vital in forming the NASICON phase. Moreover, we show that the UHS-synthesized NZLSP solid electrolyte exhibits high room temperature ionic conductivity of 7.7×10^{-4} S cm⁻¹, about three times that of the furnace-synthesized NZSP, and negligible electronic conductivity ($6.6 \times 10^{-9} \text{ S cm}^{-1}$). Additionally, no short circuit of the Na|NZLSP|Na symmetric battery occurs up to 1.4 mA cm⁻². Notably, the assembled symmetric sodium battery shows excellent stability during the Na stripping/plating processes, which can remain cycling over 4800 h at 0.1 mA cm⁻² without dendrite penetration. Our study presents an effective, time- and energy-saving pathway for the rapid synthesis of NASICON-type solid electrolytes and opens up avenues in facilitating precise and accelerated discovery of complex functional materials.

4. Experimental Section

Raw materials: All the chemical reagents such as Na₂CO₃ (99.9%, Aladdin), SiO₂ (99.9%, Aladdin), ZrO₂ (99.9%, Aladdin), Lu₂O₃ (99.9%, Aladdin), Yb₂O₃ (99.9%, Aladdin), Tm₂O₃ (99.9%, Aladdin), Er₂O₃ (99.9%, Aladdin), Gd₂O₃ (99.9%, Aladdin), Sm₂O₃ (99.9%, Aladdin), Nd₂O₃ (99.9%, Aladdin), Pr₆O₁₁ (99.9%, Aladdin), La₂O₃ (99.9%, Aladdin), Ta₂O₅ (99.9%, Aladdin), HfO₂ (99.9%, Aladdin), Nb₂O₅ (99.9%, Aladdin), Y₂O₃ (99.9%, Aladdin), ZnO (99.9%, Aladdin), MgO (99.9%, Aladdin), and NH₄H₂PO₄ (99.9%, Aladdin) were used as the starting raw materials to prepare the NASICON precursor powders. All chemicals were certified as analytical grade and used directly without any chemical treatment.

Materials Synthesis: The NASICON precursor powders Ьy mixing powders of Na₂CO₃, were prepared ZrO₂, SiO₂, Lu₂O₃/Yb₂O₃/Tm₂O₃/Er₂O₃/Gd₂O₃/Sm₂O₃/ Nd₂O₃/Pr₆O₁₁/La₂O₃/Ta₂O₅ /HfO₂/Nb₂O₅/Y₂O₃/ZnO/MgO, and $NH_4H_2PO_4$ powders in a stoichiometric ratio with 10 wt.% excessive Na_2CO_3 and $NH_4H_2PO_4$. The precursor powders were then ball-milled (QM-3SP2-CL) at 600 rpm in isopropyl alcohol for 12 h. After drying overnight at 80 °C, the precursor powders were pressed into pellets (MSK-YLJ-E60T) with a diameter of 10 mm, and then directly synthesized into pellets with the NASICON phase via the UHS technique under appropriate conditions. The UHS experimental setup was composed of two parallel strips of carbon heating element (Fuel Cell Earth), which were fixed on the holder. The high-temperature reaction process was implemented with an energy input from the direct current (DC) power supply (StarPower, 1800 W) through the holder to the carbon heating element. The carbon heating element as the Joule heating source could be ramped to a high temperature in seconds by controlling the DC power supply. All UHS processes were conducted in an Ar-filled glovebox. The temperature of the heater was calculated from the UV-vis spectra measured with a Vision Research Phantom Miro M110 high-speed camera with an error bar of $\approx \pm$ 100 °C. For the NASICON SSEs, the as-prepared pellets were sintered at 1200 $^{\circ}$ C in a box furnace for 12 h, which were then polished with 1000, 2000, and 5000 mesh sandpapers and stored in a glovebox for electrochemical tests.

To provide a basis for comparison, pristine NASICON-type NZSP SSEs was prepared using a conventional solid-phase synthesis process in a box furnace with the same compositions and excess Na/P where appropriate. An additional powder bed was used to compensate for the Na/P loss during the regular furnace synthesis. First, the pristine NZSP precursor powders were ball-milled at 600 rpm in isopropyl alcohol for 12 h, followed by overnight drying at 80 °C. The dried powder was then calcined at 900 °C to release volatile products from the starting materials. Finally, the control NZSP pellets were sintered at 1200 °C in a box furnace for 12 h. Similarly, the control NZSP pellets were polished with 1000, 2000, and 5000 mesh sandpapers and stored in a glovebox for electrochemical tests.

Materials Characterizations: X-ray diffraction analysis (XRD) was conducted using a Rigaku Smartlab 9 KW X-ray diffractometer with Cu K α radiation (45 kV, 200 mA), and 2 θ ranging from 10° to 80°. Scanning electron microscope (SEM) images were obtained using a Sigma 300 field emission SEM instrument with energy-dispersive X-ray spectroscopy (EDS). For the transmission electron microscopy (TEM) investigation, the samples were thoroughly ground into powders and diluted in ethanol by ultrasonic treatment for 5 min. The suspension liquid was dripped onto holey carbon-coated Cu grids. The high-resolution transmission electron microscopy (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (EDS) experiments were performed using an FEI Talos F200X G2 microscope equipped with Bruker windowless EDX detector at an accelerating voltage of 200 KV.

Electrochemical Measurements: Ionic conductivity was measured using AC impedance analysis (BioLogic VMP3 potentiostat). The frequency applied ranged from 7 MHz to 1 Hz with an amplitude of 10 mV. A thin layer of Pt was sputtered on each surface of the pellets as blocking electrodes. Ionic conductivity was calculated based on the following Equation: $\sigma_t = \frac{L}{R_s S}$, where σ_t , L, S, and R_t represent the ionic conductivity, thickness of electrolyte pellets, electrolyte pellet surface area, and resistance value. Activation energies were calculated from the slope of the resulting Arrhenius plot. Electronic conductivity was examined by DC polarization experiment with a DC voltage of 0.5 V, and Pt was also sputtered on both sides of the pellets. Galvanostatic stripping-plating of the Na|NASICON|Na symmetric cells was recorded at room temperature with a current density of $0.1\ mA\ cm^{-2}.$ Na metal was ultrasonically attached on the surface of the solid electrolyte pellet using an ultrasonic household cleaner.^[27] The solid electrolyte's critical current density (CCD) was evaluated by assembling Na|NASICON|Na symmetric cell using an automatic battery tester system (Neware Technology Limited) at room temperature, which was tested by rate cycling under an initial current density of 0.1 mA \mbox{cm}^{-2} with an increasing step of 0.1 mA cm^{-2} .

Theoretical Calculations: The bond valence site energy (BVSE) method was an effective simulation method to identify ionic migration channels from a static structure model.^[61] The BVSE calculations were performed using the CCNB code.^[62] The resulting isosurfaces reflect the locations in the unit cell suitable for Na⁺ which were corresponding to the Na⁺ migration channels. The cutoff radius and the grid resolution were set to 10 and 0.1 Å, respectively. The migration channels were visualized by VESTA visualization package.^[63] The calculation workflow was managed by the high-throughput computational platform for battery materials.^[64]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

ionic conductivity, NASICON structure, rapid synthesis, sodium-metal batteries, solid-state electrolytes

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