Fabrication of thin sheets of the sodium superionic conductor Na5YSi4O12 with tape casting

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**Abstract**

All-solid-state sodium batteries (ASSNBs), which combine the benefits of high safety and low cost, are expected to be an alternative or complementary storage technology to lithium ion batteries. Herein, we developed an aqueous tape casting technique for the continuous fabrication of ceramic sheets made of silicate-based Na5YSi4O12 (NYS) Na+ ion superionic conductor for the first time. After sintering, the ceramics showed a total conductivity of 1.0 mS cm-1 at room-temperature, low total activation energy of 0.30 eV, and wide electrochemical window of over 8 V. The critical current density of NYS tape against Na-metal electrodes can reach 2.2 mA cm-2 and the galvanostatic cycling time is over 280 h under 0.8 mA cm-2 and 0.8 mAh cm-2. The obtained tape has high crystalline purity, dense microstructure, favorable mechanical properties (hardness *H* of 2 GPa and elastic modulus *E* of 45 GPa). This work not only highlights the potential of the scarcely studied silicate-based NYS ionic conductor as a functional separator, but also presents a cost-efficient and eco-friendly continuous fabrication using the aqueous tape casting technique, thus being expected to boost the practical application of NYS as solid-state electrolyte in ASSNBs.

**Keywords**: Na5YSi4O12, sodium superionic conductor, thin sheets, aqueous tape casting.

**1. Introduction**

Solid-state battery (SSB) technologies can become a game-changer in consideration of their improved safety and energy densities enabled by the implementation of thin and robust ceramic solid-state electrolytes (SSEs). [1-4] However, SSBs encounter challenges in terms of incompatibility with established assembly lines dedicated to lithium-ion battery (LIB) production, [5] of different cell configurations and lack of electrolytes with high conductivity and stability. [6-9]

Despite the overwhelming success of LIBs in research and industrialization over the past three decades transferring human life into the “wire-free era”, [10, 11] LIBs possess inherent limitations regarding cathode capacity and electrochemical stability window of electrolyte. [12-14] In contrast, the congener sodium attracts attention due to its comparable physicochemical properties, abundant deposits and availability as well as the lower costs of raw materials. [15-19] Hence, the all-solid-state sodium battery (ASSNB), an alternative or complement of lithium-based batteries, is one of the prime candidate in the field of electrochemical energy storage. [20] In addition to developing excellent cathode materials, [21] decreasing the mass or thickness of the SSEs while ensuring their ionic transport and separator functions is another effective strategy for ASSNBs to reach or even surpass existing LIBs in energy density. [22-25]

Tape casting of ceramics, firstly patented by Howatt in 1952 for the preparation of thin capacitor sheets, [26] is suitable for both the thickness-adjustable (usually 10~1000 for the green tape) and the continuous fabrication of the ceramic products. It is one of the primary techniques for the large-scale ceramic manufacturing used in applications like porous membranes, electronic substrates, wear-resisting plates, capacitors, and SSE-supported batteries and fuel cells today. [27, 28] However, the tape casting method usually utilizes highly volatile non-aqueous solvents. Many efforts have been undertaken in recent decades towards improving the application of tape casting using aqueous solutions and natural products as alternatives for the frequently toxic solvents and binders, driven by environmental and health concerns. [29] Especially in the battery field, Ye *et al.* have successfully fabricated Li7La3Zr2O12 (LLZO) electrolytes by using an aqueous tape casting technique. [30, 31] Although the room-temperature ionic conductivity ( = 0.15 mS cm-1) has potential for improvement, this work integrated water-soluble eco-friendly polymers as binder and plasticizer to achieve successful preparation. [32]

Compared to the studies on the production of Li+ ion-conducting SSEs at scale, there are scarce studies on the scaling-up of Na+ ion SSEs except for the commercialized Na-β/β"-Al2O3 dedicated to high-temperature Na/S batteries. Among the Na+ ion-conducting SSEs that can be found as sulfides, [33, 34] polymers [35] or oxides, [36] the latter benefit from favorable stability in air, established synthesis processing as well as desirable . Therefore oxide-based ceramic electrolytes are regarded as a superior choice for mass preparation. [37] Li and Ligon *et al.* reported the fabrication of Na-β"-Al2O3 solid electrolyte employing tape casting with a mixture of ethanol and methyethylketone (MEK) as solvents and achieved of 12 mS cm-1 and of 180 mS cm-1, respectively, [38, 39] while the synthesis of Na-β"-Al2O3 requires sintering temperature over 1600 for densification. Okubo *et al.* have prepared Na3Zr2Si2PO12 (NaSICON) with the addition of 60Na2O-10Nb2O5-30P2O5 glass (5~10 wt%) as a sintering aid and used the tape casting technique to obtain a of 0.44 mS cm-1. [40] The tedious procedure for preparation of NaSICON raw powder and the adoption of toxic toluene as solvent in tape casting restrict scale-up. [40] Another Na+ ion superionic conductor, silicate-based Na5YSi4O12 (NYS) offers a comparable and high stability with humidity, which makes it a good choice for aqueous tape casting fabrication. The facile synthesis for obtaining pure phase powders makes this material attractive as cost-effective SSEs and for up-scaling.

Herein, NYS was used for the manufacturing of ceramic sheets using the aqueous tape casting technique. An innovative sandwiched structure design used for the sintering process enabled the preparation of dense, crack-free, flat and robust tapes with different sizes and thicknesses. The sintered tapes of NYS showed decent (1.0 mS cm-1) and favorable mechanical properties (hardness *H* of 2 GPa and elastic modulus *E* of 45 GPa). X-ray diffraction (XRD) refinement and scanning electron microscope (SEM) revealed a highly pure rhombohedral phase and a dense microstructure, respectively, which explained the high room temperature conductivity of the sintered NYS sheets. The activation energy for ionic conduction, the electrochemical stability window, critical current density (CCD) and galvanostatic cycling stability were also investigated.

**2. Experimental**

**2.1 Preparation**

The calcined NYS precursor powder was synthesized with solid-state reaction by stoichiometrically mixing Na2CO3·H2O (Aldrich, 98%), Y2O3 (VWR, 99.0%), and SiO2 (Aldrich, 99%, 1~5 μm) and appropriate ball-milling of 24 h. The calcination was carried out at 950 in air for 5 h. An aqueous solution was prepared by mixing and dissolving methylcellulose (MC, Alfa Aesar), polyethylene glycol (PEG, Merck) and glycerol (Merck, 99%) in the deionized water with the assistance of stirrer (IKA, RET Basic). Then the NYS precursor powder was added into the aqueous solution. The suspension was homogenized in vacuum (ca. 104 Pa) with zirconia balls (5 mm in diameter) in a planetary mixer (Thinky, ARE-500) at 1000 rpm for 10 minutes to form a uniform slurry for tape casting. Details of the recipe have been listed in **Table 1**. The selection and optimization of the percentage content of dispersant, binder and plasticizer in the aqueous slurry in terms of the rheological behavior and the characteristics of the green tape have been reported for LLZO tapes.[30] The mixed slurry was transferred into the slurry reservoir of the tape casting machine and then cast onto a Mylar substrate foil using a height-adjustable doctor blade. Here a slit width of 0.4 mm at a blade speed of 10 mm s-1 was used. After drying overnight in ambient atmosphere, the tapes were warm-pressed at 80 °C and 120 MPa for 2 minutes to enhance the green density before the following punching, laminating and sintering steps. As the green tapes are thin and flexible, they can be punched into different diameters and be laminated into multi-layers as required (**Fig. S1**). The sintering at 1100 for 6 h resulted in densities of 2.57~2.72 g cm-3, corresponding to 90~95 % of the theoretical density (2.86 g cm-3). [41] It should be noted that in order to obtain a flat and dense tape, the green tape was placed between two NYS pellets prepared by uniaxial pressing and sintering. This sandwiched structure (**Fig. S2**), prepared with the same raw powder, effectively prevents the tape from bending and sticking to the substrate during the high temperature sintering process. Since tapes are typically thin, the sintering process requires only the gravity of the top NYS pellet (produced the pressure of ~77 Pa, see **Fig. S2** and its notes) to ensure a flat tape without pressure sintering.

Table 1. Slurry recipe for the NYS tape.

|  |  |  |
| --- | --- | --- |
| Material | Function | Mass percentage (%) |
| NYS precursor | Ceramic precursor | 32.64 |
| Deionized water | Solvent | 59.35 |
| Methylcellulose | Binder | 0.89 |
| Glycerol | Plasticizer | 3.56 |
| Polyethylene glycol | Plasticizer | 3.56 |

**2.2 Characterization**

The crystal structure of NYS was characterized by XRD using a Bruker D4 ENDEAVOR diffractometer with Cu radiation. The crystal lattice parameters of the sample were determined by the software Jana2006 program for the Rietveld refinement. [42] The microstructure of the sintered tape was analyzed using the scanning electron microscope HITACHI TM3000 and Zeiss Merlin field-emission SEM equipped with an energy dispersive spectroscopy (EDX) detector to analyze the elemental composition of samples.

The electrical conductivities were measured with two commercial electrochemical systems (Keysight E4991B and Novocontrol Technologies Alpha-A), with an AC frequency range from 3 GHz to 1 MHz and from 7 MHz to 1 Hz, respectively. In combination, impedance spectrum of the samples from 3 GHz to 1 MHz can be observed. The fitting of the impedance data was conducted by the Zview software (Scribner Associates Inc.). The as-sintered tapes were sputtered with Au on both sides for the AC impedance measurements in the frequency range from 3 GHz to 1 Hz with an alternating voltage amplitude of 5 mV. The temperature-dependent impedance was recorded between -100 and 100 to determine the activation energy ().

The electrochemical window, critical current density (CCD) and galvanostatic cycling stability were measured with an electrochemical workstation (BioLogic VMP300) equipped with climate chambers (Vötsch, VT4002) for controlling the temperature. The linear scanning voltammetry (LSV) measurement was performed in an asymmetric cell with Na as reversible electrode and Au as blocking electrode, which was assembled in a glovebox (Glovebox System, Germany) filled with Ar gas. The voltammetry range for the LSV measurement was between open-circuit voltage (2.2 V) and 8 V (vs. Na+/Na) and the scanning rate was 0.1 mV s-1. The CCD and galvanostatic cycling stability measurements were performed in a Na||NYS tape||Na symmetric cell with Na metal as reversible electrodes in a Swagelok cell. The galvanostatic cycling for testing the Na+ plating/stripping stability was performed under the constant current density of 0.8 mA cm-2.

The indentation tests were conducted at room temperature using a NanoTest Xtreme test setup from Micro Materials® (Wrexham, UK) equipped with a diamond Berkovich tip. The samples were indented at constant loading time of 10 s to maximum load. When the maximum load was reached, the load was held constant for 5 s before unloading the sample. The analysis of the data was based on an automatic procedure of the instrument following the Oliver-Pharr methodology [43] and ASTM E2546-07. [44] Modulus and hardness were derived from the load-displacement data via the determination of contact stiffness from the unloading portion. Poisson’s ratio and Young’s modulus of diamond were assumed as = 1141 GPa and = 0.07, respectively. [45]

The sintering behavior of NYS tape was measured with a 402 C dilatometer (Netzsch-Gerätebau GmbH) between 30 and 1000 in air. The heating and cooling rates during the test were 10 K min-1. The sample was prepared by isostatic pressing of an 8 mm diameter and 5 mm thickness pellet.

**3. Results and discussion**

**3.1 Preparation, crystal structure and microstructure**

The preparation process of NYS tapes consists of four steps: slurry preparation, tape casting, punching and sintering. The first step was the mixing of the slurry, comprising the NYS precursor powder, binder, plasticizer, and water as solvent. The second step was to inject the well-mixed slurry into the tape reservoir for casting and to evaporate of the solvent, where the doctor blade gap and casting speed were two parameters that significantly influence the quality of green tape. Prior to sintering, the peeled tape was punched into different shapes.

The crystal structure of tape-cast NYS was characterized by XRD (**Fig. 1a**) and the refinement demonstrated that NYS crystallized in rhombohedral phase with space group (**Fig. 1b**). The refined lattice parameters are *a* = 22.019 Å, *c* = 12.605 Å, and *V* = 5292.6 Å3, which is very close to the reported data (*a* = 22.03164 Å, *c* = 12.60818 Å) [46]. The microstructure of the NYS tape was shown in the cross-sectional and top-viewed SEM images (**Fig. 1c~d**), and the thickness of the tape was about 160 μm. The uniform elemental distribution in the NYS tape was shown in **Fig. S3**. The analysis of crystal structure and microstructure showed that the sintered tape had good crystalline phase purity and high density.



Fig. 1. Crystal structure and microstructure of NYS tape. (a) XRD pattern of sintered NYS tape (1100 for 6 h), which exhibits high crystal phase purity (Na5YSi4O12: 94.5%; Na3YSi2O7: 5.5%). (b) Projection of crystal structure of NYS from the refinement of XRD patterns along [001] direction. SEM images of the cross-section (c) and the top surface (d) of NYS. The thickness of the tape is about 160 μm and the microstructure is very dense. Fig. 1d is from the red squared area in Fig. 1c.

**3.2 Electrochemical performances**

Impedance spectrum of NYS tape and the fitted impedance profile with equivalent circuit are shown in **Fig. 2a**. The impedance spectrum can be fitted with an inductance (L0) in series with two RC elements (here R1+CPE1 and R2+CPE2) and an additional constant phase element (CPE3), in which L0 represents the inductance from the cables, R1+CPE1 ascribe to the resistance of the Na+ ionic conduction in the bulk (i.e. grain), R2+CPE2 belong to the grain-boundary processes followed by a capacitive process (CPE3) associated with the electrode polarization, i.e. the NYS tape/Au interfacial capacitance (). The total resistance of 34 Ω at RT comprised of 18 Ω for bulk resistance (R1 = =18 Ω) and 16 Ω for grain-boundary resistance (R2 = = 16 Ω), indicating that the bulk and total Na+-ion conductivities are 1.9 and 1.0 mS cm-1, respectively. The low frequency “spike” represents charge build-up at the blocking Au electrodes. [47] The attributions of each component in the equivalent circuit are summarized in **Table 2**. For comparison, the electrical and electrochemical performances of several representative Li+ and Na+ solid electrolytes are summarized in **Table 3**. The NYS tape exhibited comparable total ionic conductivity (1.0 mS cm-1) with the reported polycrystalline NYS pellet (1.59 mS cm-1). [46]



Fig. 2. Electrical and electrochemical performance of NYS tape. (a) The Nyquist plot of measured and fitted impedance spectrum for NYS tape at RT. The bulk and total resistances from the fitted data are 18 and 16 Ω, respectively. The insets show the cell configuration and the equivalent circuit used for data fitting. The Au coating is applied as blocking electrodes and Ni sheets act as current collectors on both sides of the tape. The frequency range varies between 3 GHz and 1 Hz, and the amplitude is 5 mV. The bulk and total conductivities of NYS tape are 1.9 and 1.0 mS cm-1 at room temperature. (b) Arrhenius plots of bulk and total conductivities of the NYS tape. Their activation energies calculated from the slopes of the fitted lines are = 0.27 eV and = 0.3 eV, respectively. (c) The LSV profile of NYS tape. The inset shows the configuration of the cell with Na and Au as reversible and blocking electrodes on both sides of the tape. The voltage range varies between 2.2 and 8 V, and the scanning rate is 0.1 mV s-1. (d) The profile of critical current density (CCD) measurement of NYS tape. The CCD value is 2.2 mA cm-2. The inset shows the symmetric cell configuration for the measurements of CCD and galvanostatic cycling stability with Na metal as electrodes. (e) The profile of galvanostatic cycling stability measurement. The applied current density is 0.8 mA cm-2 and the time of stable cycling is over 280 h. The inset is a magnified view of a part of the curves.

Table 2. The attributions of each component in the equivalent circuit in Fig. 2a.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Component | L0 (H) | R1 (Ω) | R2 (Ω) | CPE1 (F) | CPE2 (F) | CPE3 (F) |
| Attribution | Inductance from cables | Bulk resistance | Grain-boundary resistance | Bulk capacitance | Grain-boundary capacitance | NYS tape||Au interfacial capacitance |
| Value |  | 18 | 16 |  |  |  |
| Capacitance range from ref. [47] | / | / | / |  |  |  |

L: inductance; R: resistance; CPE: constant phase element.

Table 3. Comparison of ionic conductivity, activation energy and electrochemical stability window with representative Li+ and Na+ electrolytes, especially tape-cast samples.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Composition | Total (mS cm-1) | (eV) | Electrochemical window (V) | Refs. |
| Na3Zr2Si2PO12 (NASICON) with 60Na2O-10Nb2O5-30P2O5 glass (5-10 wt.%) tape | 0.44 | / | / | [40] |
| Na-β"-Al2O3 tape | 180 (300) | 0.29 | / | [39] |
| Na-β"-Al2O3 tape | 12 (200) | / | / | [38] |
| Poly(acrylonitrile) (PAN)+ Na3Zr2Si2PO12 composites | 0.14 | 0.33 | 4.8 (vs. Na+/Na) | [48] |
| Li1.5Al0.5Ti1.5P3O12 (Li-NaSICON) tape | 0.30 | 0.26 | / | [27] |
| Cellulose-supported PPC solid polymer electrolyte (CPPC-SPE) | 0.30 | / | 4.5 (vs. Li+/Li) | [49] |
| NYS pellet (950/8 h; 1050/36 h) | 1.59 | 0.20 | (vs. Na+/Na) | [46] |
| NYS tape (1100/6 h) | 1.0 | 0.30 | (vs. Na+/Na) | This work |

The temperature-dependent ionic conductivities plot in Arrhenius diagrams (**Fig. 2b**) and linearly fitted for the determination of the bulk and total activation energies of = 0.27 eV and = 0.30 eV, respectively, which are higher than that of the NYS pellet ( = 0.2 eV) [46] mainly influenced by high grain-boundary resistance in the NYS tape, which might be the influence of different grain-boundary conductivity of the samples prepared by different method, as well as amorphous or undesired secondary phase Na3YSi2O7 (4.5%), which are not favorable for ionic conduction.

The electrochemical stability of the NYS tape was characterized by linear scanning voltammetry (LSV, **Fig. 2c**), which suggests a stable electrochemical window up to 8 V vs. Na+/Na electrode, much higher than polymer or composite electrolytes of below 5 V [50] without significant oxidation and with the perspective to be coupled with high voltage cathodes for high energy density ASSNBs.

To investigate the feasibility of NYS tape as an electrolyte, symmetric cells with NYS tapes as electrolytes and Na metal as electrodes were assembled and tested, and their critical current density (CCD) and galvanostatic cycling stability have been shown in **Fig. 2d-e**. The CCD value of NYS tape against Na metal electrodes is 2.2 mA cm-2 and the galvanostatic cycling time is over 280 h under the current density of 0.8 mA cm-2 without apparent overpotential, which indicate a stable Na+ stripping/plating flux and show the qualification of NYS tapes as the electrolytes and functional separators in ASSNBs.

**3.3 Mechanical properties and sintering behavior**

Besides the conductivity and electrochemical window, the mechanical properties of the sintered NYS tape are of vital importance for solid electrolytes considering the planar configuration of SSBs which require pressure to ensure good contact between components for stable operation. The measurements of the hardness (*H*) and elastic modulus (*E*) of NYS tape have been performed by the nano-indentation method. The measurements are presented as nano-indentation curves with different loadings (250 and 500 mN) in **Fig. 3a**. The measured values of *E* have been evaluated according to Equation 1, which are summarized in the **Table 4**. The *H* value of the NYS tape is almost 2 GPa and the *E* is nearly 45 GPa depending on the different loading. Compared with Li1.5Al0.5Ti1.5P3O12 (LATP) and Al/Y-substituted NaSICON (see **Table 5**), NYS tape exhibited lower hardness and elastic modulus, which suggests accommodation of significant chemomechanical strain in the adjacent electrode materials and ensures a good contact between the NYS tape electrolyte and the electrode.



Fig. 3. (a) The nano-indentation curves for the loading-unloading cycles under 250 and 500 mN. The test was repeated three times for each loading force. The elastic modulus and hardness were derived from the unloading part. The inset schematically shows the indenter tip pushed into the sample. (b) Shrinkage behavior of NYS tape. The onset temperature of sintering is 890.

Table 4. Mechanical properties of NYS tape determined by nano-indentation method.

|  |  |  |  |
| --- | --- | --- | --- |
| Loading force (mN) | Indentation depth (nm) | Hardness *H* (GPa) | Elastic modulus *E* (GPa) |
| 250 | 2850 | 1.926 | 45.07 |
| 500 | 4300 | 1.797 | 39.06 |

Table 5. The comparison of synthesis, thermal and mechanical properties with representative Li+/Na+ SSEs.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Composition | Processing method | Sintering condition | Mechanical properties | Refs. |
| Na-β"-Al2O3 tape | Tape casting with ethanol/methyethylketone (MEK) as solvent. | 1600/2 h. | Ring-on-ring flexural strength: MPa. | [39] |
| Na-β"-Al2O3 tape | Tape casting with ethanol/MEK as solvent. | 1600. | / | [38] |
| Li1.5Al0.5Ti1.5P3O12 (LATP) tape | Tape casting with ethanol/MEK as solvent. | 850~1000/1 h. | Nano-indentation:  *E*: 109 GPa;  *H*: 8.7 GPa. | [27] |
| Na1+2xAlxYxZr2-2x(PO4)3 and Na3+2xAlxYxZr2-2x(SiO4)2(PO4) pellets | Pechini method. | 1150~1200/5~10 h. | Indentation:  *E*: 72~82 GPa;  *H*: 4.8~5.8 GPa. | [51] |
| NYS tape | Aqueous tape casting. | Onset for shrinkage: 890; 1100/6 h. | Nano-indentation:  *E*: 45 GPa;  *H*: 2 GPa. | This work |

The elastic modulus of the NYS tape can be correlated with the equivalent modulus according to the unloading curve by using

(1)

where and are the elastic modulus and Poisson’s ratio of the indenter material, respectively. A diamond indenter was used in the measurement and the parameters are = 1141 GPa and = 0.07 (given by equipment parameters). is the Poisson’s ratio of the sample, which is assumed to be 0.25 (derived from the reported NaSICON materials due to the chemical similarity of NYS and NaSICON). [45] The shrinkage behavior of NYS tape was recorded in a dilatometer and is shown in **Fig. 3b**. The onset temperature for shrinkage is 890.The most favorable sintering conditions for obtaining the dense NYS tape is 1100 for 6 h, which is lower than conventional NaSICON (generally over 1200) or Na-β/β"-Al2O3 electrolytes (over 1500) (see **Table 4**). The shrinkage is about 15~19% in x-y plane (i.e. in diameter for round tapes), yet 1~4% in z-axis (i.e. in thickness) (see **Table S1**). The shrinkage along the z-axis is not significant due to the uniaxial pressing of the tape.

**3.4 Fabrication of thin NYS tapes employing the tape casting technique**

As one of the mature technologies for ceramic materials processing, tape casting is expected to be integrated into the production and fabrication lines for solid-state battery materials, thus fostering the development and industrialization of all-solid-state batteries. **Fig. 4a** shows a green tape of NYS produced by tape casting, which has uniform thickness of 50 μm, high flatness, and good ductility for easy trimming and stacking, which allows flexibility in tuning the size and thickness of electrolytes. **Fig. 4b** exhibits a picture of sintered tapes having a very flat and uniform shape. The translucent feature illustrates the good densification of the thin NYS ceramic tapes (~120 μm). The NYS tape was prepared by aqueous tape-casting after a simple ball-milling and calcining to produce the NYS precursor powder, which is relatively facile and inexpensive compared to other ionic conductor tapes, both in terms of raw materials and processing cost (see **Table S2**). The thin electrolyte sheets obtained by tape casting can facilitate the industrialization of SSBs.

C:\Users\a.yang\Desktop\Picture1.tif

Fig. 4. Digital pictures of (a) the green tape and (b) the translucent sintered NYS tapes.

After screening for interface-compatible cathodes or modifying of the cathode/electrolyte interface, the tape casting technique can be used for the continuous preparation of laminated configurations of electrolyte/interface/cathode, thus facilitating the production of NYS electrolytes or ASSNBs.

**Conclusions**

This work demonstrated the fabrication of silicate-based NYS electrolytes using an aqueous tape casting technique, which exhibited good Na+ ion conductivity ( = 1.0 mS cm-1) and mechanical properties (hardness *H* of 2 GPa and elastic modulus *E* of 45 GPa), low activation energy for Na+ ion migration ( = 0.30 eV), and a wide electrochemical stability window (over 8 V vs. Na+/Na). The high CCD value up to 2.2 mA cm-2 and stable galvanostatic cycling performance over 280 h under the current density of 0.8 mA cm-2 and the capacity of 0.8 mAh cm-2 verify the advantages of NYS tape as a qualified solid electrolyte. The aqueous tape casting technique promises environmental and operational safety and low preparation cost in scaling-up, which pioneers an eco-friendly way for the continuous preparation of self-supported Na+ ion SSEs.

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