

## Supplementary Information

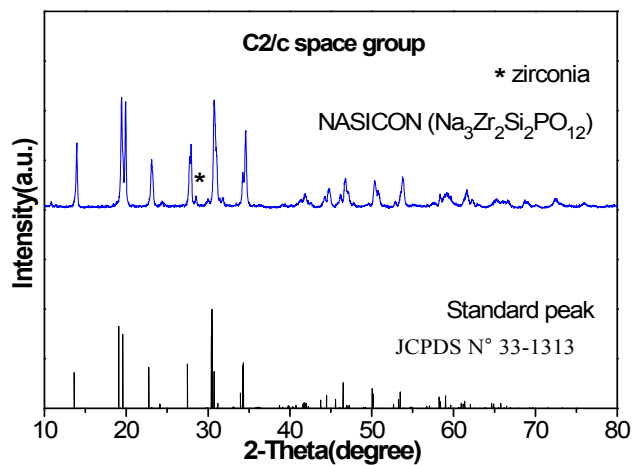
### Hybrid solid electrolyte for flexible solid-state sodium battery

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**Fig. S1.** XRD data for NASICON ( $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ ) ceramic powder.

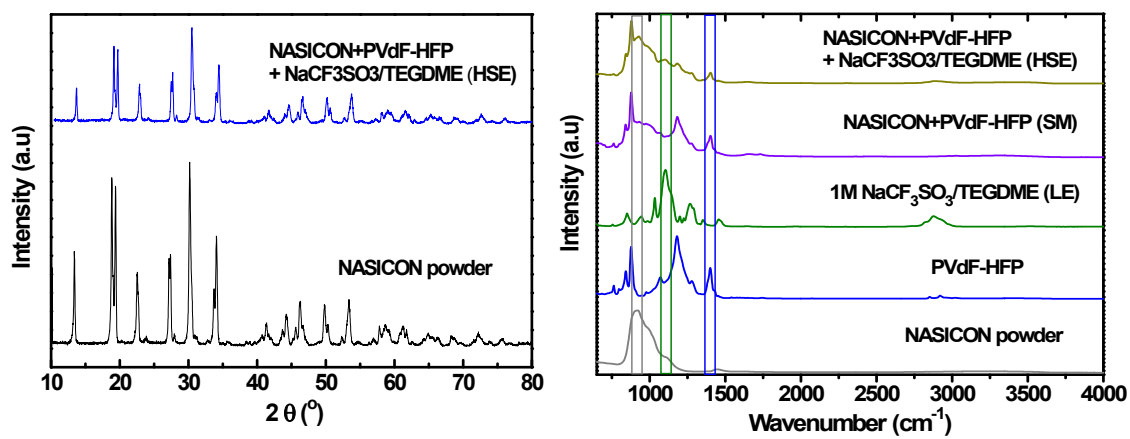
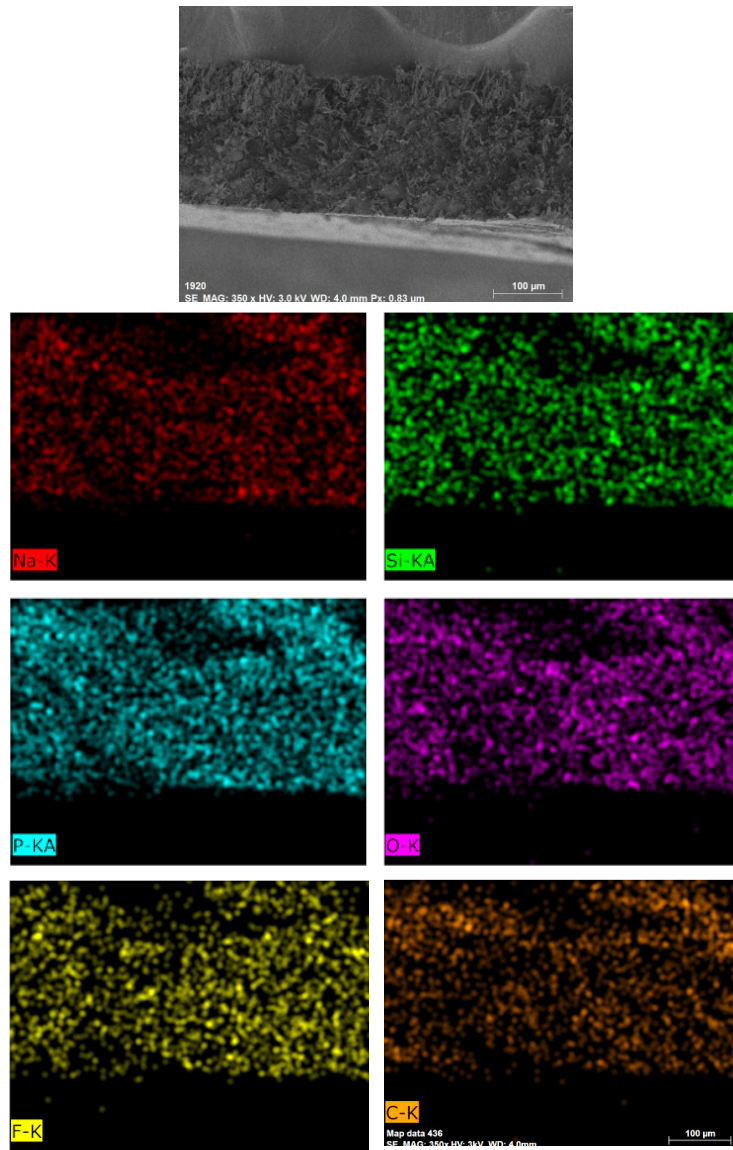
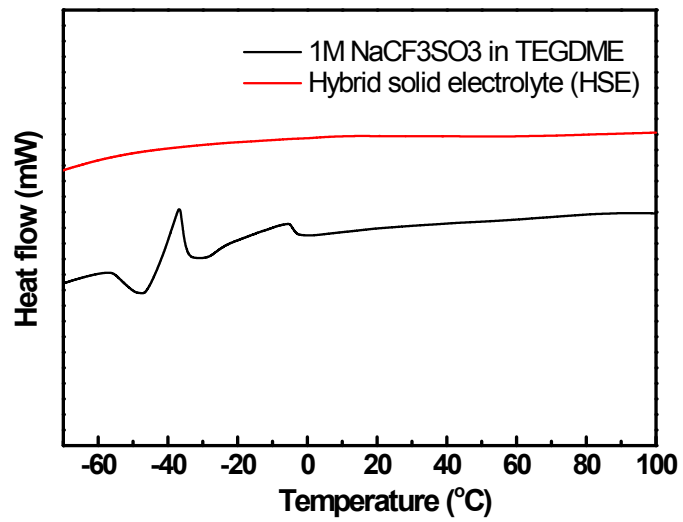


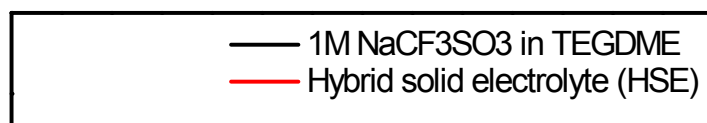
Fig. S2 XRD and FR-IR spectra of HSE, NASICON, PVdF-HFP and liquid electrolyte (1M NaCF<sub>3</sub>SO<sub>3</sub> in TEGDME).



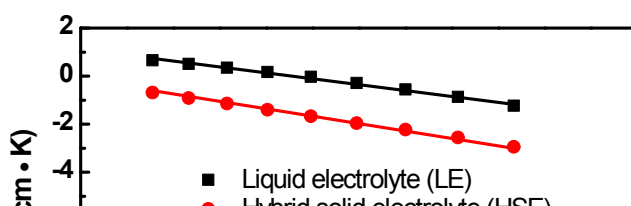
**Fig. S3** EDX mappings of cross-sectional HSE with Na, Si, P, O, F, and C atoms.



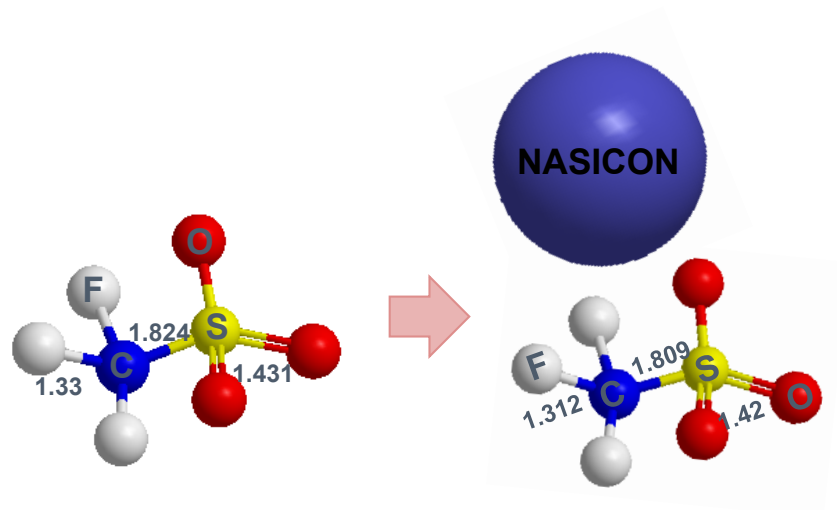
**Fig. S4** DSC trace of liquid electrolyte and HSE. Scan rate: 10 °C min<sup>-1</sup>.



**Fig. S5** RT Raman spectra of liquid electrolyte and HSE showing symmetrical  $\text{SO}_3$  bending mode for free  $\text{CF}_3\text{SO}_3$  and  $\text{CF}_3\text{SO}_3$  coordination to Na ions at 25 °C.

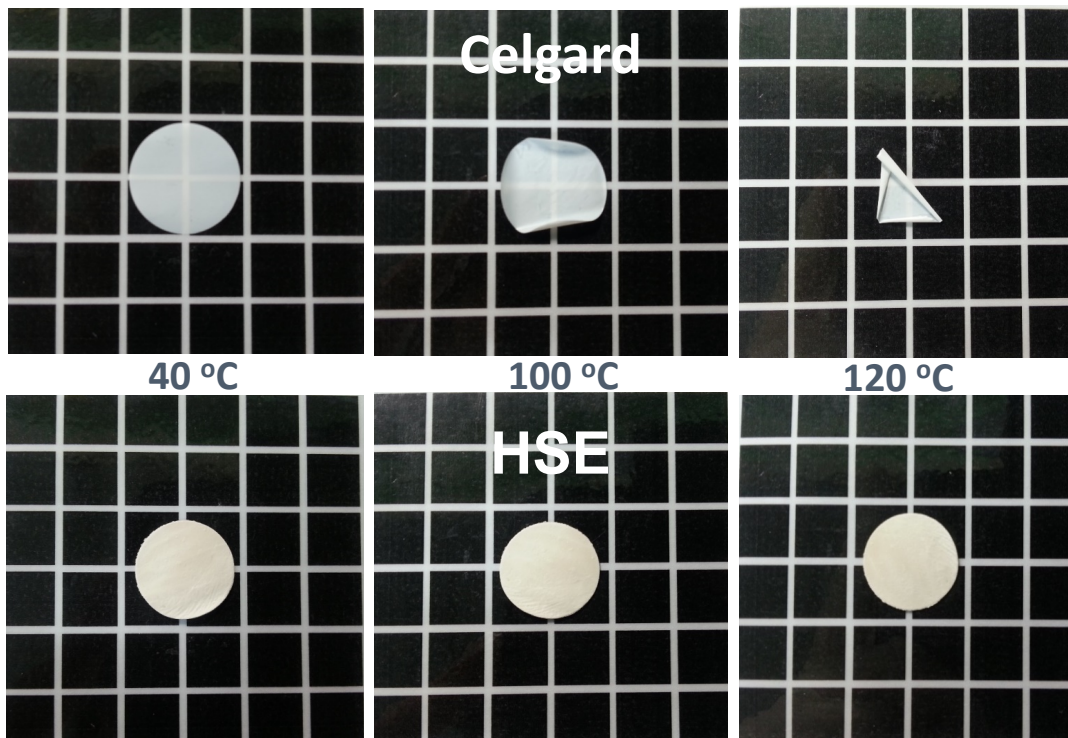


**Fig. S6** Arrhenius plots of total conductivities of liquid electrolyte (1M NaCF<sub>3</sub>SO<sub>3</sub> in TEGDME), solid film, and HSE.



**Fig. S7** Bond lengths ( $\text{\AA}$ ) of free  $\text{CF}_3\text{SO}_3$  anions and  $\text{CF}_3\text{SO}_3$  anions interacted with NASICON particle.





**Fig. S8** Shrinkage of commercial membrane (Celgard) and HSE at various temperatures.

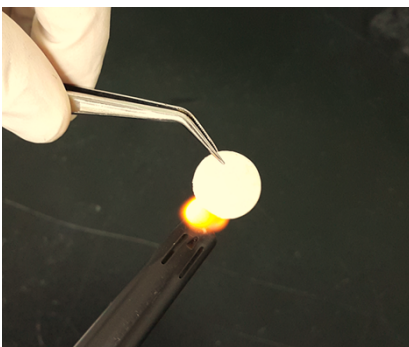
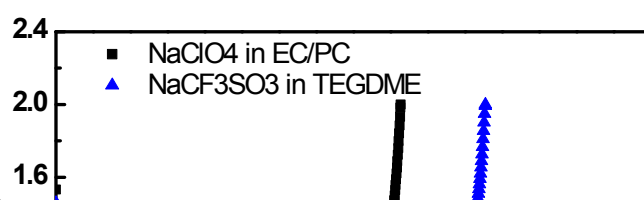
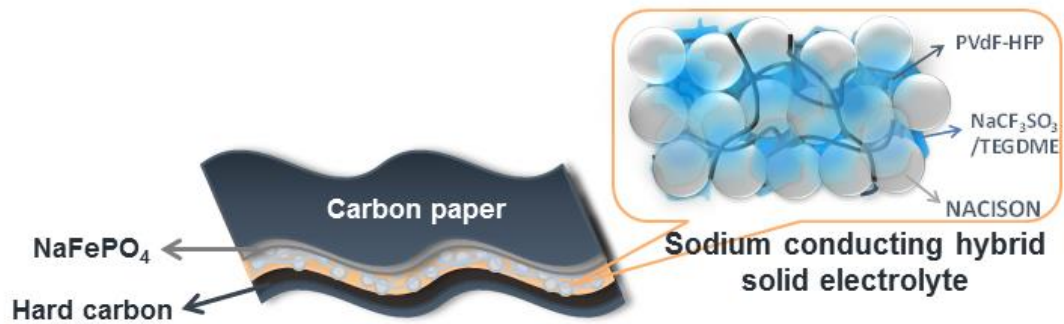


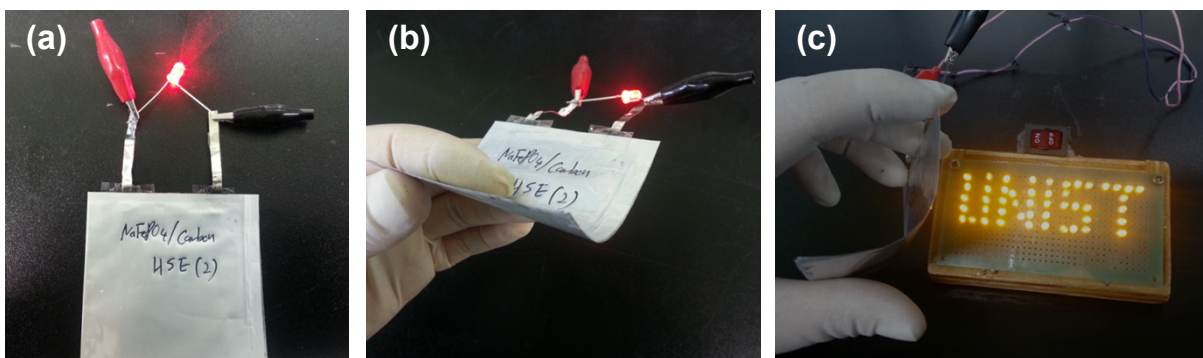
Fig. S9 The combustion test of HSE.



**Fig. S10** Discharge and charge voltage curves of Na/hard carbon cell with two different electrolytes at room temperature (0.2 C-rate).



**Fig. S11** Flexible solid-state Na battery scheme with Na-conducting HSE.



**Fig. S12** Photographs showing electrical states (a: normal static condition, b: bending, c: following repeated bending) of red LED lamps connected to flexible solid-state Na batteries fabricated with HSE.

**Fig. S13** Short-term cycling of flexible solid-state Na cell with Na-conducting and non-Na-conducting HSE at different C-rates (10 cycles at each C-rate, 25 °C, 1.5–4.0 V).