

Supporting Information

High ionic conducting rare-earth silicate electrolytes for sodium metal batteries

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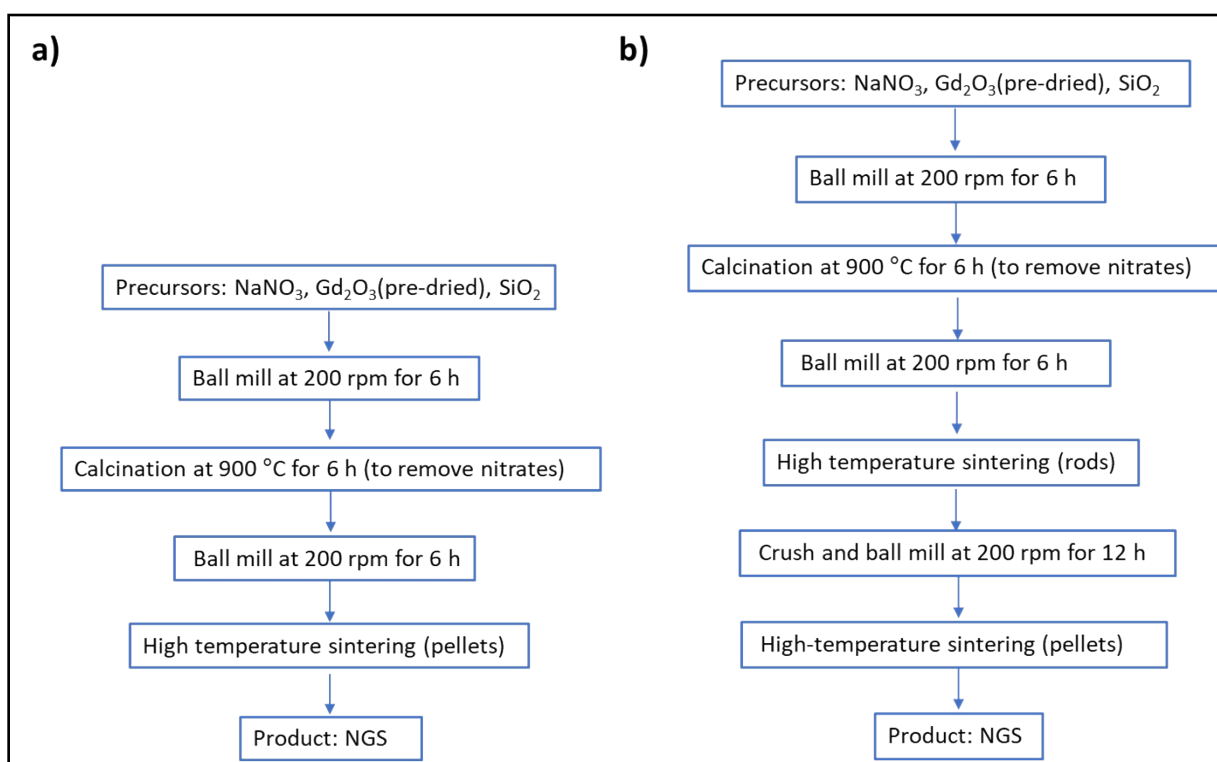


Fig. S1 Solid-state synthesis method. a) Route 1 and b) Route 2, respectively.

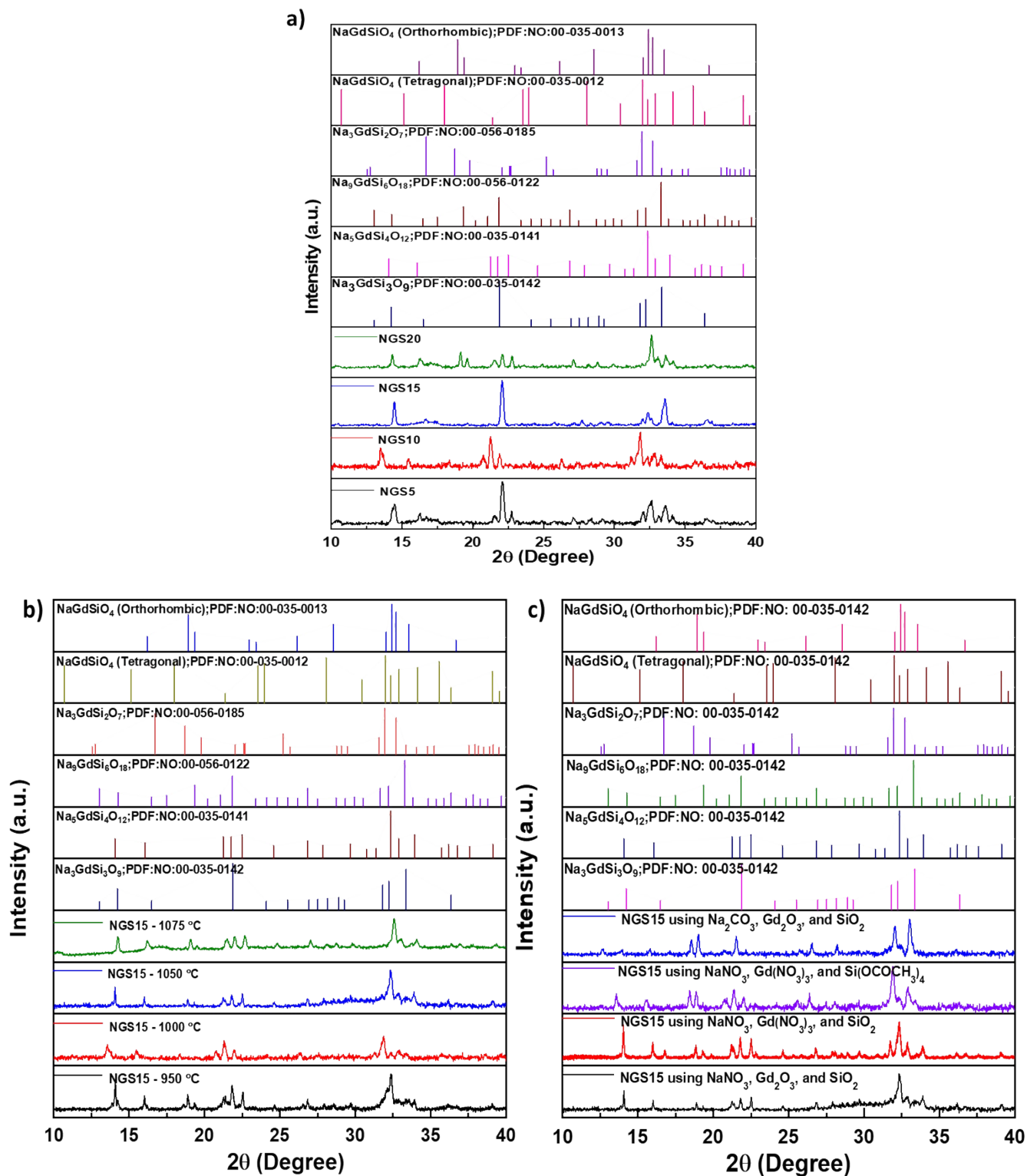


Fig. S2 PXRD patterns along with the reference patterns of Na₃GdSi₃O₉ (PDF: 00-035-0142), Na₅GdSi₄O₁₂ (PDF: 00-035-0141) (Rhombohedral), Na₉GdSi₆O₁₈ (PDF 00-056-0122), Na₃GdSi₂O₇ (PDF: 00-056-0185) (hexagonal), NaGdSiO₄ (Orthorhombic phase; PDF: 00-035-0013), and NaGdSiO₄ (Tetragonal phase; PDF: 00-035-0012). (a) NGS5-NGS20 prepared by Route 2, (b) NGS15 sintered at different temperatures (950, 1000, 1050, and 1075 °C) (Route 1), and (c) NGS15 synthesized using various precursors (Route 1).

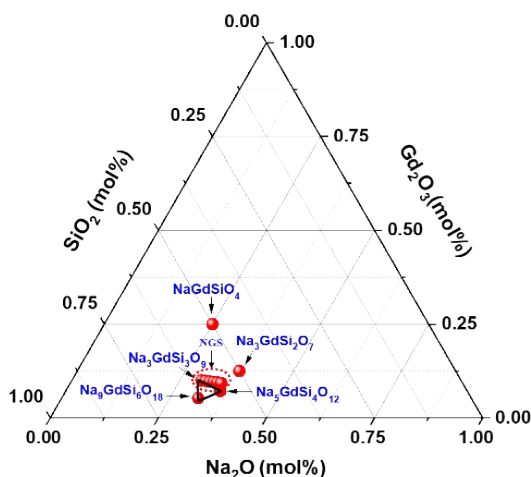


Fig. S3 Phase diagram of the system $\text{Na}_2\text{O} - \text{Gd}_2\text{O}_3 - \text{SiO}_2$ with NaGdSiO_4 , $\text{Na}_3\text{GdSi}_2\text{O}_7$, $\text{Na}_3\text{GdSi}_3\text{O}_9$, $\text{Na}_3\text{GdSi}_4\text{O}_{12}$ and $\text{Na}_3\text{GdSi}_6\text{O}_{18}$ phases identified in the diagram. NGS with six compositions we prepared also circled.

Table. S1 Comparison of all silicates with their sintering conditions and ionic conductivity. (All the samples were sintered at 1050 °C for 6 h unless specified).

No	Sample	Sintering routes	Conductivity (S cm^{-1}) (25 °C)
1.	NGS0 ($3\text{Na}_2\text{O} - \text{Gd}_2\text{O}_3 - 6\text{SiO}_2$)	Route 1	10^{-6}
2.	NGS5 ($3.15\text{Na}_2\text{O} - \text{Gd}_2\text{O}_3 - 6\text{SiO}_2$)	Route 1	6.27×10^{-4}
		Route 2	1.2×10^{-5}
3.	NGS10 ($3.3\text{Na}_2\text{O} - \text{Gd}_2\text{O}_3 - 6\text{SiO}_2$)	Route 1	6.3×10^{-4}
		Route 2	3.31×10^{-4}
		1075 °C (Route 1)	3.64×10^{-4}
4.	NGS15 ($3.45\text{Na}_2\text{O} - \text{Gd}_2\text{O}_3 - 6\text{SiO}_2$)	950 °C (Route 1)	8.7×10^{-5}
		1000 °C (Route 1)	3.6×10^{-4}
		Route 1	6.8×10^{-4}
		Route 1 – using $\text{Gd}(\text{NO}_3)_3$	6.18×10^{-4}
		Route 1 – using $\text{Gd}(\text{NO}_3)_3$ and silicon tetraacetate	1.4×10^{-4}
		Route 1 – using Na_2CO_3	1.94×10^{-5}
		Route 2	4.59×10^{-4}
		Route 2 (12 h)	4.63×10^{-4}
		Route 2 (24 h)	4.57×10^{-4}
		1075 °C (Route 1)	7.25×10^{-4}
5.	NGS20 ($3.6\text{Na}_2\text{O} - \text{Gd}_2\text{O}_3 - 6\text{SiO}_2$)	Route 1	5.7×10^{-4}
		Route 2	4.7×10^{-4}
		1075 °C (Route 1)	5.9×10^{-4}
6.	NGS25 ($3.75\text{Na}_2\text{O} - \text{Gd}_2\text{O}_3 - 6\text{SiO}_2$)	Route 1	10^{-8}

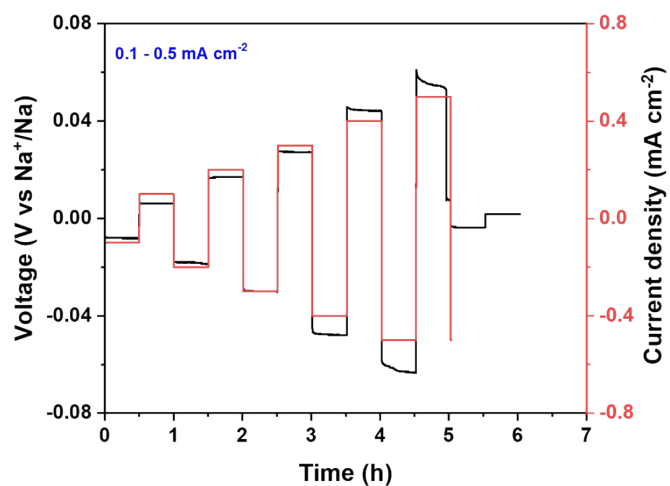


Fig. S4 Critical current density (CCD) of the Na|NGS15|Na symmetric cell at 25 °C.

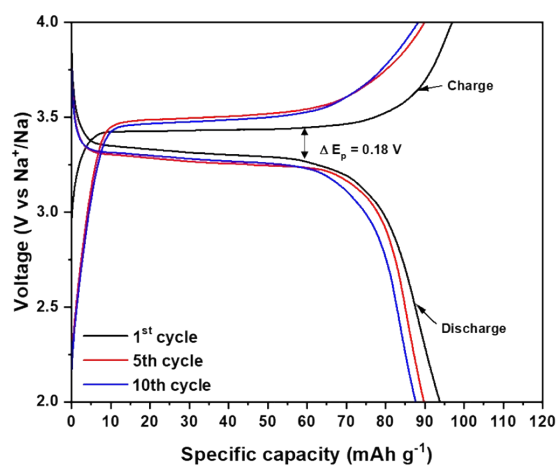


Fig. S5 Galvanostatic charge-discharge curves of 1st, 5th and 10th cycle of a Na|NGS15|15 μ L of 1M NaClO₄ in PC: FEC |NVP battery at 0.1C at 25 °C. (NGS15 was prepared via Route 1).

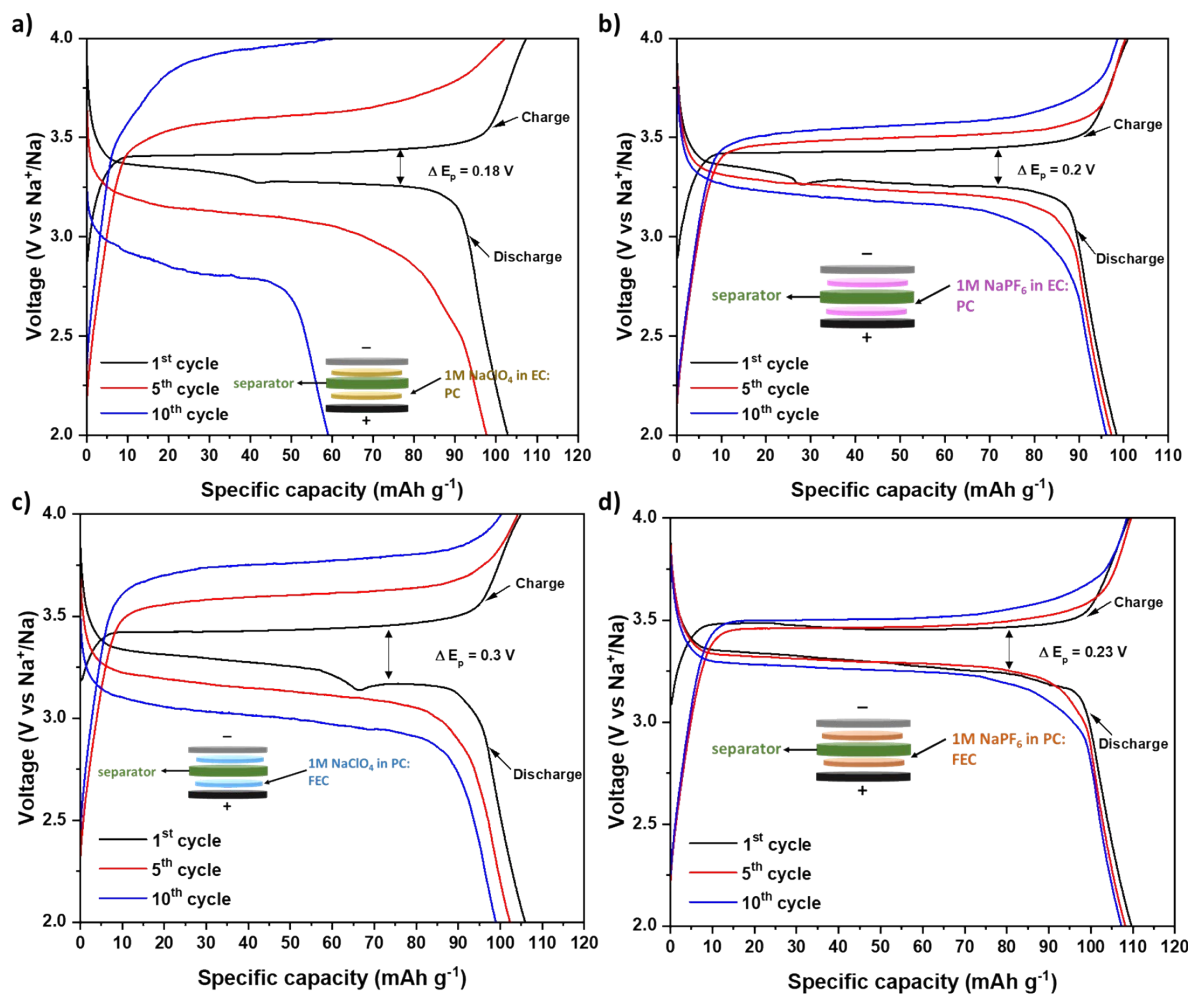


Fig. S6 Galvanostatic charge-discharge curves of 1st, 5th and 10th cycle at 0.1C at 25 °C. (NGS15 was prepared via Route 1). (a) Na|40 μ L of 1M NaClO₄ in EC: PC|separator|40 μ L of 1M NaClO₄ in EC: PC |NVP, and (b) Na|40 μ L of 1M NaPF₆ in EC: PC|separator|40 μ L of 1M NaPF₆ in EC: PC |NVP, (c) Na|40 μ L of 1M NaClO₄ in PC: FEC|separator|40 μ L of 1M NaClO₄ in PC: FEC |NVP, (d) Na|40 μ L of 1M NaPF₆ in PC: FEC|separator|40 μ L of 1M NaPF₆ in PC: FEC |NVP.

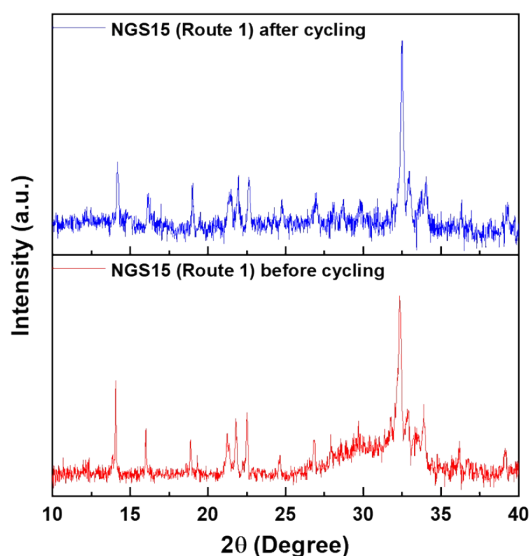


Fig. S7 XRD patterns of NGS15 solid electrolyte before and after battery testing.

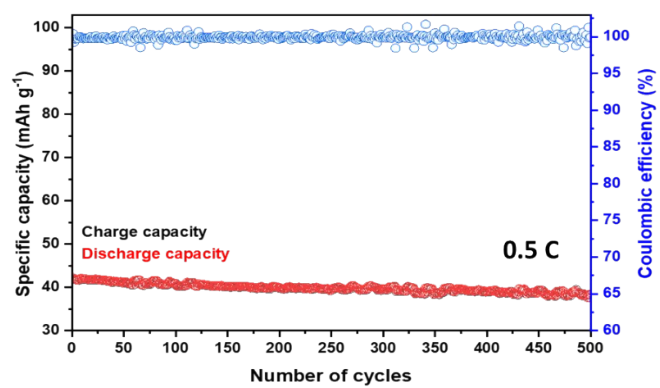


Fig. S8 Long-term stability of hybrid battery for 500 cycles at 0.5 C.