Electronic Supplementary Information

Reversibly Transformation between Solid and Liquid States of $Na_2S_2O_3 \cdot 5H_2O$ as Supercapacitor Electrolytes with Low Volatilization and Low Self-Discharge

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Content

1. Experimental Section

1.1 Fabrication of active carbon electrode for symmetrical supercapacitor

The nickel foam with a 12 mm diameter was the current collecting substrate. The activated carbon slurry is composed of 0.1608 g activated carbon as the active component, 0.0326 g acetylene black as the conductive additive and 0.0218 g polyvinylidene fluoride as a polymer binder, 5 drops of N-methyl pyrrolidone solvent. Before coating the slurry on the nickel foam, the following two tasks are completed: first, a record of the mass of the nickel foam m_1; second, mix the slurry by ball milling or grinding. The nickel foam coated with activated carbon slurry was heated at 120 °C for 1 h to remove the solvent. After the nickel foam with activated carbon slurry is cooled to room temperature, the weight was recorded as m_2. The amount of active carbon is calculated to be about 0.009863 g (m_2-m_1).

1.2 Thermal fabrication of supercapacitor based on liquating $Na_2S_2O_3$ in $5H_2O$ electrolyte

To be able to turn $Na_2S_2O_3 \cdot 5H_2O$ into a liquid state to facilitate the encapsulation of supercapacitors, each process must be kept at ~65°C. First, the 2032 positive shell loaded with activated carbon electrodes was transferred to a heating plate at 65 °C. $Na_2S_2O_3 \cdot 5H_2O$ was placed in an oven at 65 °C to make it turn to liquid. 2 drops of hot sodium thiosulfate liquid were added to the hot positive shell. The separator with a diameter of 16 mm is laid on the positive electrode to prevent short circuits of the positive and negative electrodes. Then the activated carbon electrode and the negative shell are placed rapidly on the separator in turn. After the supercapacitor encapsulator was heated to a temperature of 65 °C with a high-power dryer, the loose cell based on positive shell/activated carbon/electrolyte/separator/electrolyte/activated carbon/negative shell was immediately transferred to a hot encapsulator and sealed at a pressure of 0.9 MPa.

1.3 **Materials characterization**

Powders XRD pattern were collected using Cu Kα radiation (λ = 1.54 Å) operating at 45 kV and 200 mA equipped with a 2D matrix high-speed detector moving from 5 to 80 degrees with 0.01-degree step (Rigaku Smartlab diffractometer). The morphology of the solid $Na_2S_2O_3 \cdot 5H_2O$ electrolyte was imaged by SEM operating at 10 kV and 43 pA emitter current with a 4.5 mm working distance (Thermo Fisher Scientific FIB-SEM GX4). The element content and element mapping of the solid $Na_2S_2O_3 \cdot 5H_2O$ electrolyte were measured on an energy dispersive spectrometer (EDS, Bruker) equipping on SEM via detecting element X-ray emission intensity excited by electron beam operating at 10 kV and 43 pA.

1.4 **Electrochemical characterization**

The charge-discharge and self-discharge performance of the supercapacitor was recorded on the instrument of Wuhan LAND measurement (CT3001A, Wuhan LAND Electronic Co. Ltd). The charge-discharge conditions were as follows: voltage range of 0−0.5 V and a current density of 0.067 $mA \cdot mg^{-1}$. The two-electrode cyclic voltammetry (CV) test was recorded on an electrochemical workstation (Jiangsu Donghua Analytical Instrument Co., Ltd, DH7003), active carbon on Ni foam as working electrodes, 2 M $Na_2S_2O_3$, 2 M KOH, and liquated $Na_2S_2O_3$ dissolved in $5H_2O$ as the electrolyte. Test conditions were as follows: voltage range of 0−0.5 V and different scanning speeds (from 0.005 to 0.05 $V \cdot s^{-1}$). Electrochemical impedance spectroscopy was collected on an electrochemical workstation (Jiangsu Donghua Analytical Instrument Co., Ltd, DH7003) with a frequency range from 10^6 to 0.05 Hz. The electrochemical test at high temperature is carried out by placing the supercapacitor in an oven setting with a target temperature.

2. Results

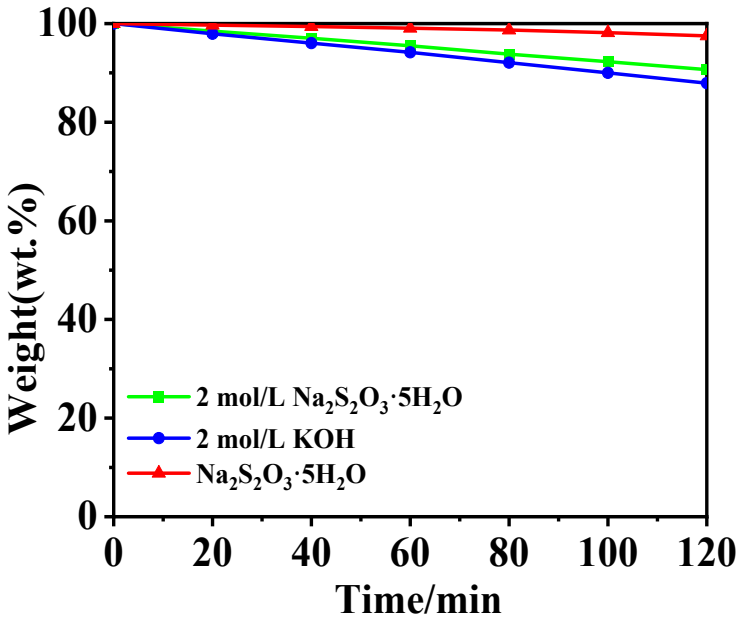

Figure S1: Weight loss based on 2 M $Na_2S_2O_3$ electrolyte, 2 M KOH electrolyte, and liquating $Na_2S_2O_3$ in $5H_2O$ at 80 ℃ for 2 h.

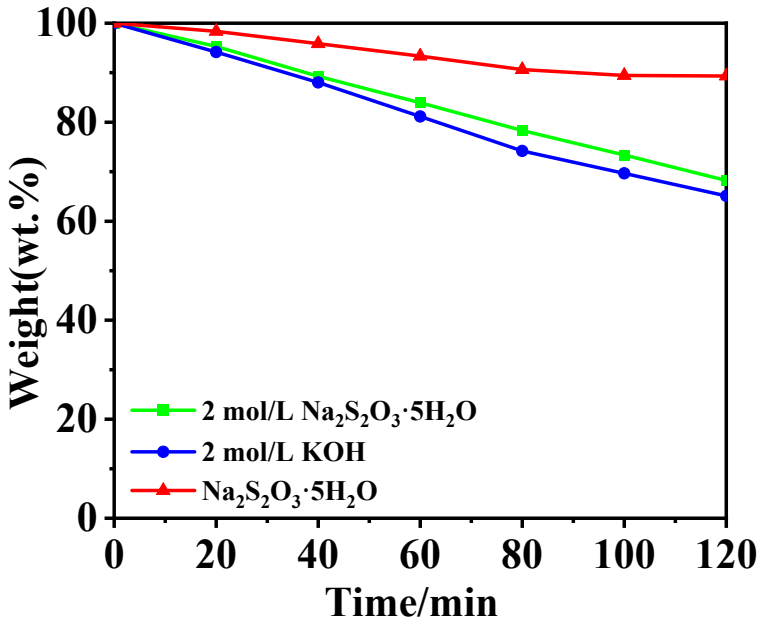

Figure S2: Weight loss based on 2 M $Na_2S_2O_3$ electrolytes, 2 M KOH electrolyte, and liquating $Na_2S_2O_3$ in $5H_2O$ at 120 ℃ for 2 h.

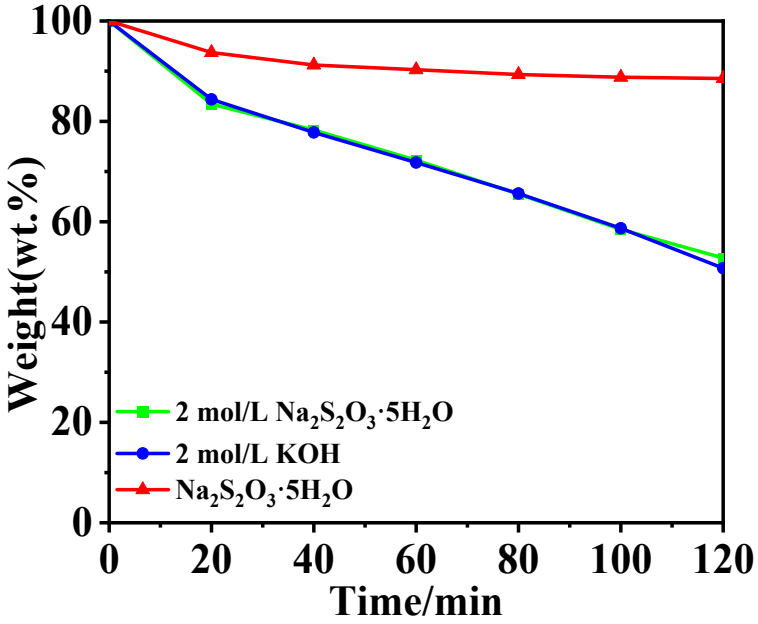

Figure S3: Weight loss based on 2 M $Na_2S_2O_3$ electrolytes, 2 M KOH electrolyte, and liquating $Na_2S_2O_3$ in $5H_2O$ at 140℃ for 2 h.

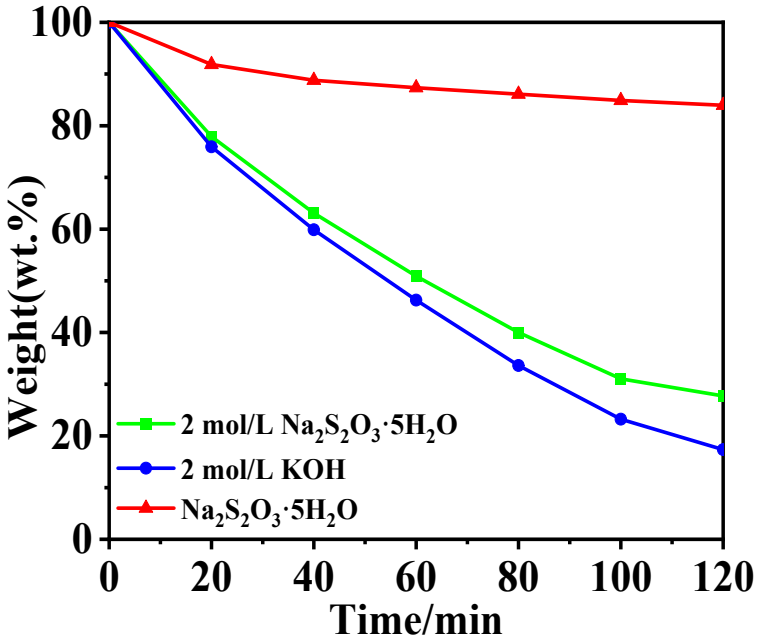

Figure S4: Weight loss based on 2 M $Na_2S_2O_3$ electrolytes, 2 M KOH electrolyte, and liquating $Na_2S_2O_3$ in $5H_2O$ at 160 °C for 2 h.

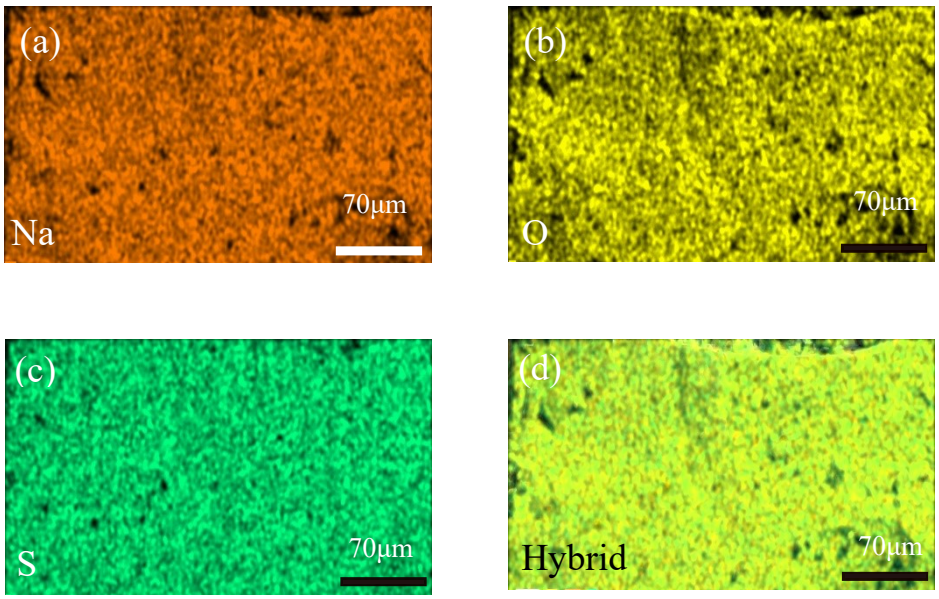

Figure S5: Element mapping: (a) Na element of $Na_2S_2O_3$; (b) O element of $Na_2S_2O_3$; (c) S of element $Na_2S_2O_3$; (d) hybrid element of $Na_2S_2O_3$.

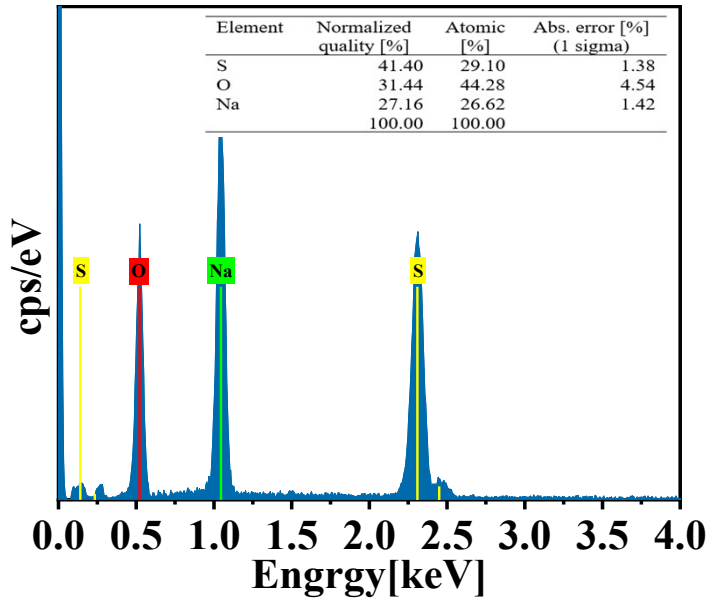

Figure S6: Element content and EDS of $Na_2S_2O_3$.

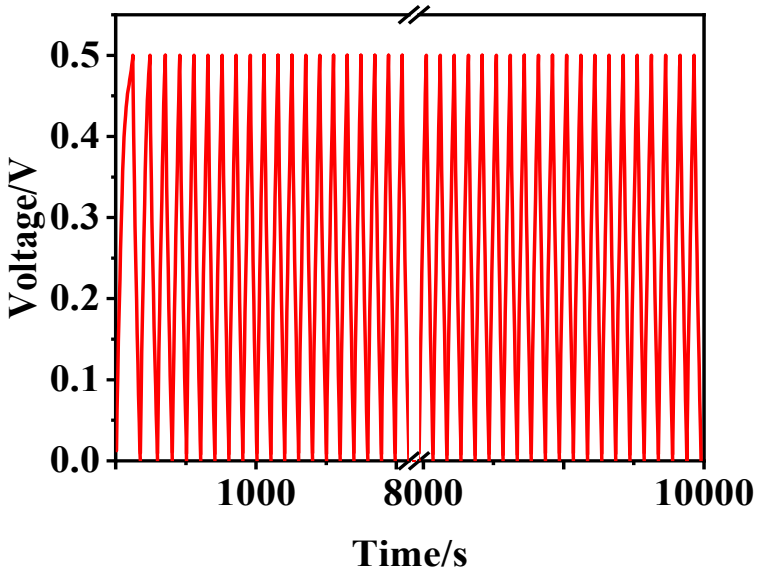

Figure S7: Cyclic stability of supercapacitor with 2 M $Na_2S_2O_3$ electrolyte at 25 ℃ at a current density of 0.067 $mA \cdot mg^{-1}$.

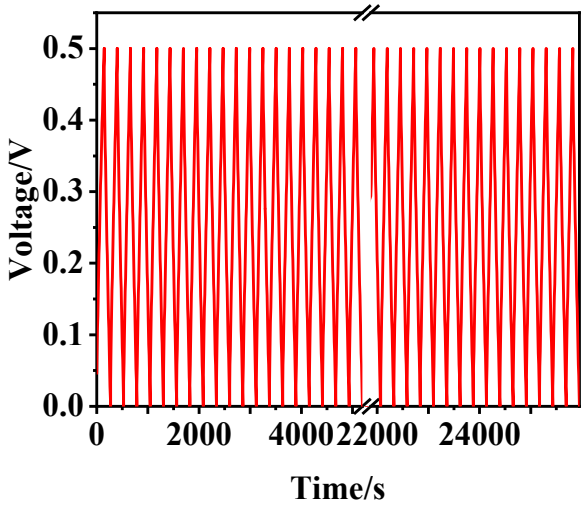

Figure S8: Cyclic stability of supercapacitor with 2 M KOH electrolyte at 25 ℃ at a current density of 0.067 $mA \cdot mg^{-1}$.

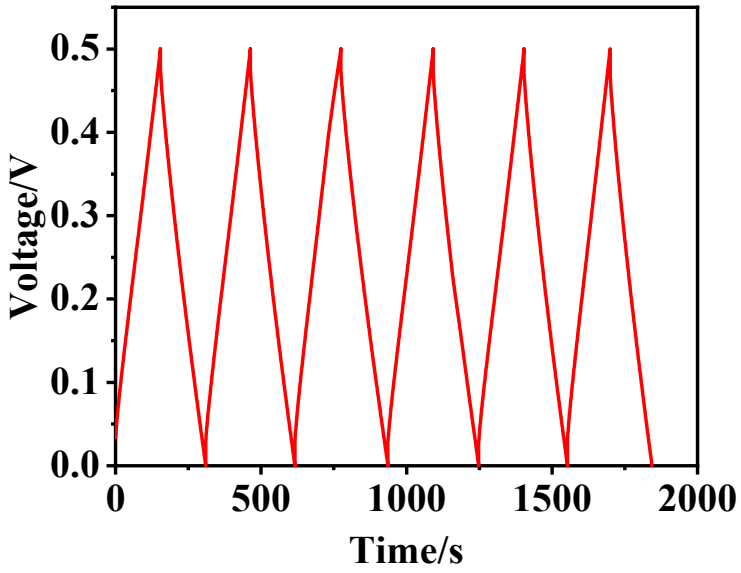

Figure S9: Cyclic stability of supercapacitor with 2 M KOH electrolyte at 65 ℃ at a current density of 0.067 $mA \cdot mg^{-1}$.

Table S1: The first and last columbic efficiency of supercapacitors with 2 M $Na_2S_2O_3$ and liquating $Na_2S_2O_3$ in $5H_2O$ electrolyte at 65 ℃.

Electrolyte	Temperature/℃	Coulombic efficiency%	
		the first	the last
2 M $Na_2S_2O_3$	65	89.95	92.91
$Na_2S_2O_3$ dissolved in $5H_2O$		81.38	82.41

Table S2: Specific energy, power, and specific capacitance of supercapacitors with different electrolytes at 25 and 65 ℃.

Electrolyte	Temperature /℃	Specific energy /Wh·kg^{-1}	Power /W·kg^{-1}	Specific capacitance / mF·cm^{-2}
2 M $Na_2S_2O_3$	25	0.14	10.52	110.40
	65	0.31	10.52	246.11
2 M KOH	25	0.30	8.39	299
	65	0.36	8.39	359.52
$Na_2S_2O_3$ dissolved in H_2O	25	0.000676	2.43	0.88
	65	0.50	10.98	377.21