Supplementary Information

**High Performance Sodium-Sulfur Battery at Low Temperature Enabled by Superior Molten Na Wettability**

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Experimental Methods

**BASE disc fabrication**

BASE discs were fabricated using a vapor phase process, as described previously. Starting powders were high purity \( \alpha-Al_2O_3 \) (Almatis 16-SG, >99.8%) and yttria-stabilized zirconia (YSZ, Imerys Fused Minerals, 5.4 wt% \( Y_2O_3 \)). A mixture of 70 vol% \( \alpha-Al_2O_3 \) and 30 vol% YSZ was ball milled with a dispersant (Phospholan PS-131, AkzoNobel), solvents (methyl ethyl ketone/ethanol, 4:1), a plasticizer (benzyl butyl phthalate, Alfa Aesar, 98%) and a binder (polyvinyl butyral, Butvar® B-79) to make slurry. After the slurry was cast into a thin sheet (~125 \( \mu \)m), the sheets were laminated and laser-cut to form discs. The discs were fired at 1600 °C in air to achieve full density (>99%). The sintered \( \alpha-Al_2O_3/YSZ \) discs were then placed in loose \( \beta''-Al_2O_3 \) powder with 10% NaAlO\(_2\) and heat treated at 1400 °C for 10 h in air in order to convert \( \alpha-Al_2O_3 \) into \( \beta''-Al_2O_3 \). The \( \beta''-Al_2O_3 \) powder used in the conversion process was synthesized using boehmite, \( Na_2CO_3 \), and \( Li_2CO_3 \) via a solid-state reaction. The conversion occurred by a coupled transport of sodium and oxygen ions from the \( \beta''-Al_2O_3 \) powder to the samples. The thickness and diameter of the converted composite \( \beta''-Al_2O_3/YSZ \) discs are ~500 \( \mu \)m and ~26 mm, respectively.

**Wettability study**

To study the Na wetting behavior on BASE, an aqueous solution of saturated LAT \[\text{Pb(OAc)}_2\cdot3\text{H}_2\text{O}, \text{Sigma Aldrich}, >99\%\] was drop-cast on the surface of the BASE samples and the samples were then heat-treated at various temperatures (400, 450, 500, or 550 °C) under nitrogen gas atmosphere (flow rate: 75 cc/min). The treated BASEs were then transferred into a nitrogen-filled glove box (oxygen and H\(_2\)O levels less than 0.1 ppm). The samples were placed on a hot plate at 120 °C and a solidified drop of liquid sodium was transferred to the surface of the BASEs. The wetting behavior and contact angle were studied after the wetting was stabilized, up to 30 minutes.

**Cell construction**

A BASE disc was glass-sealed to an \( \alpha-Al_2O_3 \) ring, as described previously. A helium leak test was performed to confirm no leakage from the glass-sealed BASE. The surface of BASE facing the anode side was then coated with LAT aqueous solution and heat-treated at various temperatures, as mentioned above. The treated samples were transferred into the glove box for the subsequent cell assembly.

Cathode raw materials were pretreated in a glove box before use. Sulfur (Alfa Aesar, 99.999%) and \( Na_2S_4 \) (Alfa Aesar, 90+%%) were heat-treated at 90 and 200 °C under vacuum for 24h, respectively. The liquid catholyte was prepared by dissolving 1 mol NaI in tetraglyme at room temperature. The tetraglyme was ordered from Novolyte Technologies and dried with pre-activated 4 Å molecular sieves (Aldrich) to remove the moisture. After the 0.6 g of tetraglyme (4G) was heated to 120 °C, a mixture (0.1 g) of S and \( Na_2S_4 \) with the mole ratio of 4:1 was added into the 4G solution, which was stirred for 2 h. At the meanwhile, the heat-treated BASE/\( \alpha-Al_2O_3 \) ring was preheated to the same temperature. After the solution was poured into the cathode
chamber, a carbon felt was inserted into the cathode chamber as a current collector. A foil and a spring made of Mo were placed on the top of the cathode as a current collector. After 60 mg of sodium (slightly more than stoichiometric amount) was preloaded into anode chamber of the cell, a spring-loaded stainless-steel shim, which served as a molten sodium reservoir, was inserted into the compartment. Anode and cathode end plates were then compression-sealed to both sides of $\alpha$-Al$_2$O$_3$ ring using two polymer rings (fluorinated ethylene propylene for the cathode side and polyvinylidene fluoride for the anode side). The active area of the typical cells used in this work is 3 cm$^2$.

**Cell testing**

The assembled cells were heated in air to 120 °C for testing. The galvanostatic discharge/charge test was carried out with a BT-2000 Arbin battery testing system. The cells were initially discharged down to 1.1 V at 1 mA (~0.33 mA/cm$^2$). The cells were then charged back to cut-off voltage of 2.3 V under the same current. After the initial charge/discharge, the cells were cycled under various current densities with the voltage limits of 2.3 and 1.1 V. For long-term cycling tests, a current of 14 mA (4.67 mA/cm$^2$) was employed for both the charge and discharge.

**Scanning electron microscopy (SEM)**

The morphological features of the lead acetate products on the BASE surfaces after heat treatment at various temperatures were analyzed with a JEOL JSM-5900LV scanning electron microscope. Energy-dispersive X-ray spectroscopy (EDX) analysis was performed for obtaining the elemental mappings on an Oxford Instruments system.

**X-ray Photoelectron Spectroscopy (XPS)**

XPS measurements were performed using a Physical Electronics Quantum 2000 Scanning ESCA Microprobe, which has a focused monochromatic Al Ka X-ray (1486.7 eV) source and a spherical section analyzer. The samples were prepared in the nitrogen purged glove box and later was transferred into an Ar purged glove box attached to the XPS system. Then, the sample was loaded into an XPS detection chamber from the Ar purged glove box to avoid any exposure to air during the sample handling process. The depth profile of Pb XPS spectra were obtained by applying the sputtering conditions described as follow. 2kV monoatomic Ar$^+$ ions at ~2μA current were used to sputter the surface of the Pb particles. The focused ion beam was rastered over a 3 mm$^2$ area of the sample at an incident angle of 45°. Each cycle corresponds to ~2.5 nm of sputtered material based on a calibrated sputter rate from a known thickness of SiO$_2$/Si reference material.
Table S1. Specific capacity calculation for different S cathode formula

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Cathode (charge state)</th>
<th>Theoretical Capacity based on cathode active material (mAh/g)</th>
<th>Theoretical Capacity (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2\text{Na} + \text{2S} = \text{Na}_2\text{S}_2)</td>
<td>S</td>
<td>835.8</td>
<td>486.8</td>
</tr>
<tr>
<td>(2\text{Na} + \text{Na}_2\text{S}_4 = 2\text{Na}_2\text{S}_2)</td>
<td>\text{Na}_2\text{S}_4</td>
<td>307.6</td>
<td>243.4</td>
</tr>
<tr>
<td>(\text{Na} + \text{Na}_2\text{S}_4/\text{S} (1/4) = \text{Na}_2\text{S}_2) (Current work)</td>
<td>\text{Na}_2\text{S}_4/S=1/4</td>
<td>531.6</td>
<td>365.1</td>
</tr>
</tbody>
</table>

Overall reaction of Na-S battery demonstrated in this work can be described as follow:

\[
6\text{Na} + \text{1Na}_2\text{S}_4 + 4\text{S} = 4\text{Na}_2\text{S}_2 \quad (\text{Na}_2\text{S}_4/S=1:4 \text{ in mol ratio}) \quad (1)
\]

To have a better comparison with previous results, the theoretical capacities are calculated considering cathode active materials only (\(\text{Na}_2\text{S}_4 + 4\text{S}\));

\[
\text{Q} = \frac{nF}{(3600*\text{MW})} \text{mAh/g},
\]

where \(n = 6, F = 96485.3329, \text{MW} = (22.989*2 + 32.065*8) = 302.5\)

\[
\text{Q} = 6*96485.3329/(3600*302.5)*1000 = 531.6 \text{mAh/g}
\]

If we consider the total mass of active materials, then the molecular weight is 440.4 (from equation 1), and corresponding \(\text{Q} = 6*96485.3329/(3600*440.4) = 365.1 \text{mAh/g}\)
Fig. S1. Specific Energy Density of LAT-550 cells at 120°C for 1000 cycles.
Fig. S2. On the left, SEM images of the BASE surfaces treated at 400, 450, 500, and 550 °C. The corresponding Pb EDX maps on the right confirm the composition of spherical particles as Pb. All scale bars correspond to 2 μm.