Electronic Supplementary Information

A High Energy Density All Solid-State Tungsten-Air Battery

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Phase diagram of W-O system

According to phase diagram of W-O system of Fig.S1, W-WO₂ is considered as the redox couple for energy storage within the temperature window of interest.

![Phase diagram of W-O system](image)

Figure S1 Phase diagram of the tungsten-oxygen system [1]

Experimental

Preparation of redox couple materials

The functional redox precursor WO₃ in the energy storage unit was purchased from Fisher
Chemicals. The commercial WO₃ was first ball-milled into fine particles, followed by mixing with a microcrystalline cellulose pore-former (type NT-013, FMC Corp.) in a volume ratio of 1:1. Rectangular bars were then pressed from the powders and sintered at 1100°C for 2h. All heat treatments were conducted in open air. The final granules in 9-16 mm² by 2 mm were obtained from the sintered bars. For the baseline iron-air battery, similar volume of Fe₂O₃-ZrO₂ precursor granules were used for comparison purpose. The composition and synthesis method of Fe₂O₃-ZrO₂ redox precursor were detailed in ref. [2].

**Battery assembly**

A simple planar button cell configuration was employed for the battery test, the schematic of which is shown in ref. [3]. The commercial NextCell Electrolyte Supported Button Cell (Fuel Cell Materials, Ohio, USA) was used as the RSOFC (Diameter: 20mm, effective area: 1.32cm²). Pt mesh and Silver paste were used as current collectors for both air-electrode and fuel-electrode, respectively. A specially formulated glass-ceramic was used as the hermetic sealant for battery test.

**Testing profile**

During heating, the starting material WO₃ granules were first reduced with a protective gas of 5%H₂-N₂+3%H₂O. As WO₃ gradually reduced into W/WO₂, a pure H₂ was introduced to finally reduce WO₂ into metallic W before the electrical cycle starts. The anode chamber was then closed, following by applying a small discharge current to oxidize W to WO₂ so as to establish the W-WO₂ equilibrium. The overall process was constantly monitored by the OCV of the cell. The
equilibrium OCV is roughly 1.06 V at 800°C. As soon as the cell OCV reaches 1.06V, the electrical cycle starts.

**Maximum charge density**

Due to the fact that the effective density of the redox-couple varies with the state-of-charge of the battery, the basis for evaluating the charge density also varies. Fig.S2 shows the difference in the charge densities calculated based on metal and metal oxide. It is evident that choosing metal oxide as the basis for charge density is a conservative way, which was done for the manuscript.

![Graph showing comparison of maximum charge density between Fe and W systems using different densities of ESU at 800°C.](image)

**Morphological Examination of Tungsten air Battery**

Fig. S3 shows the morphologies of W-based ESU before (a) and after test(b). It is evident that both pre-and post-test redox materials were porous. The post-tested ESU is a mixture of W and
WO₂. A distinct feature is that the grain size of post-test redox materials is smaller. The fine grains are likely to originate from the H₂/H₂O-mediated redox reaction. Fig. S3 (c) shows the post-tested RSOFC, in which the anode is detached from the electrolyte. The delamination occurred during the destructive post-test disassembling process.

Fig. S3 Morphologies of W-based ESU (a) pre-test; (b) post-test; and (c) the cross-section view of a post-tested RSOFC.

Reference
