Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

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

Xuan Zhao, Xue Li, Yunhui Gong, Nansheng Xu, Kevin Romito and Kevin Huang *

Department of Mechanical Engineering, University of South Carolina, Columbia, SC29201

Phase diagram of W-O system

According to phase diagram of W-O system of Fig.S1, W-WO_2 is considered as the redox couple for energy storage within the temperature window of interest.

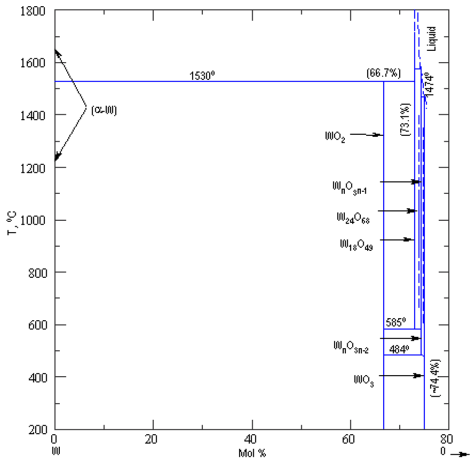

Figure S1 Phase diagram of the tungsten-oxygen system [1]

Experimental

Preparation of redox couple materials

The functional redox precurosr WO_3 in the energy storage unit was purchsed from Fisher

Chemicals. The commercial WO_3 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. Rectanglar bars were then pressed from the powders and sintered at 1100^{o}C for 2h. All heat treatments were conducted in open air. The final granules in 9-16 mm^2 by 2 mm were obtained from the sintered bars. For the baseline iron-air battery, similar volume of Fe_2O_3-ZrO_2 precursor granules were used for comparison purpose. The compostion and synthesis method of Fe_2O_3-ZrO_2 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: 1.32cm^2). 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 WO_3 granules were first reduced with a protective gas of 5%H_2-N_2+3%H_2O. As WO_3 gwas radually reduced into W/WO_2, a pure H_2 was introduced to finally reduce WO_2 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 WO_2 so as to establish the W-WO_2 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 denisty 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 chosing metal oxide as the basis for charge density is a conservative way, which was done for the manuscript.

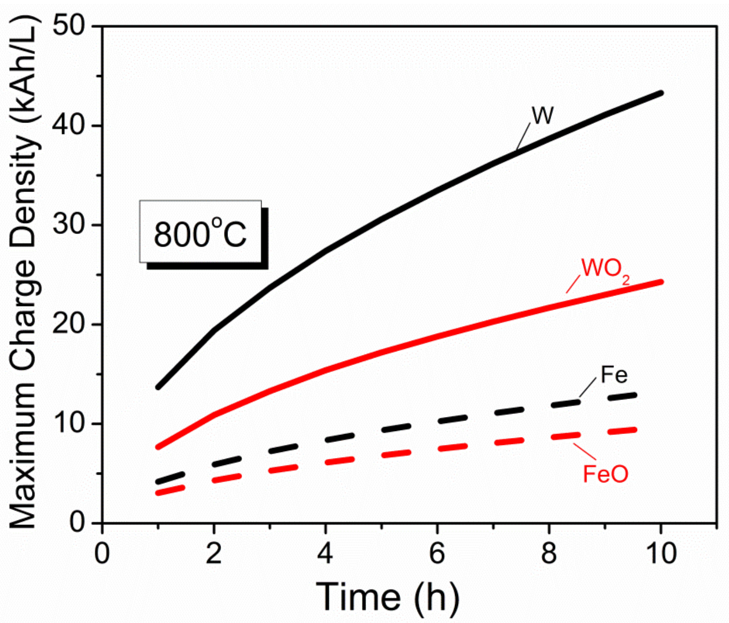

Fig.S2 Comparison of maximum charge density between Fe and W systems using different densities of ESU

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

WO_2. A distinct feature is that the grain size of post-test redox materials is smaller. The fine grains are likely to originate from the H_2/H_2O-mediated redox reaction. Fig.S3 (c) shows the post-tested RSOFC, in which the anode is detached from the electrolyte. The delamination occurred duing the destructive post-test disassembling process.

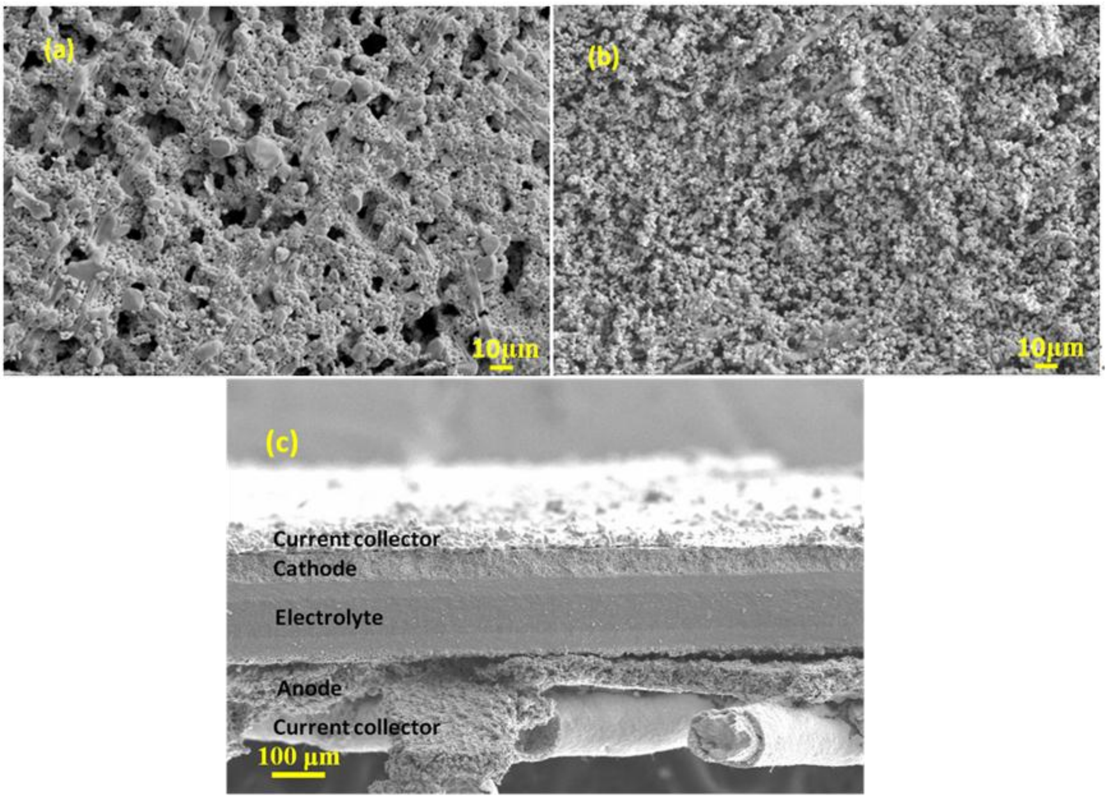

Fig. S3 Morphologies of W-based ESU (a) pre-test; (b) post-test; and (c) the cross-section view of a post-tested RSOFC.

Reference

[1] H. A. Wriedt, *Bulletin of Alloy Phase Diagrams* **10**, 368-384 (1989)

[2] N. Xu, X. Li, X. Zhao, J.B. Goodenough, K. Huang, *Energy & Environmental Science* **4** (2011) (12) 4942.

[3] X. Zhao, N. Xu, X. Li, Y. Gong, K. Huang, *RSC Advances* (2012).