Electronic Supplementary Information

Energy Storage Characteristics of a New Rechargeable Solid Oxide Iron-air Battery

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Experimental

Preparation of Fe-FeO redox powders

The Fe-FeO redox powders were synthesized from a co-precipitation method described in ref.¹. Such prepared powders have a better redox reversibility and thermal stability than those synthesized from conventional mechanical mixing method.

Battery assembly

A simple planar button cell configuration was adopted for the battery test, the schematic of which is shown in Figure S1. A commercially available NextCell Electrolyte Supported Button Cell (Fuel Cell Materials, Ohio, USA) was used as the RSOEC (Diameter: 20mm, effective area: 0.88cm²). Table S1 gives the composition and thickness of the functional layers in the RSOEC. The energy storage redox materials were packaged in form of granules underneath the ROSEC. Pt mesh and Pt paste were used as current collectors for both air-electrode and fuel-electrode. A

specially formulated glass-ceramic was used as the hermetic sealant for the battery

cell.



Fig. S1. A planar button cell configuration for testing rechargeable solid oxide Iron-air battery

| Component | Composition | Thickness (µm) |
|-------------|--------------------------------|----------------|
| Anode | Ni-YSZ/Ni-GDC(interlayer) | 50 |
| Electrolyte | Hionic ZrO ₂ -based | 150(+/-15) |
| Cathode | LSM/LSM-GDC(interlayer) | 50 |

Table S1 Compositions and dimension of the commercial NextCells²

Testing procedure

The redox material Fe₂O₃-ZrO₂ (5-10 wt%) granules were first reduced with a cover

gas of 5%H₂-N₂. Before each electrical cycle, a pure H₂ was used to finally reduce Fe_2O_3 into metallic Fe. A small current was then applied to oxidize Fe into FeO so as to create the Fe-FeO energy storage redox couple. The RSOEC's EMF was closed monitored during the initial electrochemical oxidation. As soon as EMF reached 0.97 volts, the electrochemical oxidation was stopped, and the system is ready for electrical cycles. During electrical cycles, the reaction gas was circulated in a closed-loop to homogenize the concentration. To prevent condensation, all pipelines were heat-wrapped and kept at 110°C.

A Solartron 1260/1287 Electrochemical System was employed to measure the electrical performance of the battery with software modules such as OCV (open circuit voltage)-t, impedance spectroscopy, potential-dynamic, galvanic square waves and galvanic cycles.

Other characterization

A field emission scanning electron microscope (FESEM, Zeiss Ultra) equipped with an EDS capability was employed to observe microstructures and analyze the local chemical compositions of the Fe-FeO redox materials as well as RSOEC. The phase composition of the Fe-FeO redox material was also examined by powder X-ray diffraction (PXRD) using an X-ray diffractometer (D/max-A, Rigaku, Japan) with graphite-monochromatized CuK α radiation (λ =1.5418 Å). The XRD scan was

performed at a rate of 5° min⁻¹ from 2θ = 10° to 90°, the spectrum of which was analyzed with the JADE (MDI) software to identify phase compositions. The pore characteristics of the porous Fe-containing redox unit including median pore diameter, and porosity were analyzed by a mercury porosimeter (Autopore IV, Micromeritics) in a pressure range of 0.5-30000 psi.

Microstructure of after-test fuel cell

The cross-sectional view as a FESEM image of a RSOEC after a 2-week test is shown in Fig. S2. The anode interlayer appears to be separated from the electrolyte. While this detachment certainly contributes to the anode degradation, other reasons such as electrochemical condensation of $FeO_{(s)}$ under a high steam condition are currently being investigated in our group. Fig. S3 shows EDS analysis results of the fuel-electrode near the electrolyte/fuel-electrode interface. In addition to the constituents of the fuel-electrode, a small amount of Fe (~0.14 at%) was found. This finding is a direct evidence of electrochemical condensation of $FeO_{(s)}$ proposed as the degradation mechanism in this study.



Fig. S2 SEM microstructure of RSOEC after a 2-week test



Fig.S3 EDS spectrum and compositions of the fuel-electrode after a 2-week test

Morphology of Fe-FeO redox powders

The overall performance of the solid oxide iron-air battery is determined not only by RSOEC, but also by Fe-based redox materials. Therefore, we also characterized the microstructure and porosity of Fe-based redox material to determine whether the sintering is problematic to a sustainable battery performance. Fig.S4 shows the morphology of Fe-based redox materials before (a) and after 2-week test (b). It is evident that both pre- and post-test redox materials were porous. A distinct feature is that many nanoparticles (~200 nm) were observed in the post-test sample (see Fig. S4(d)). The EDX analysis of these nanoparticles shows a chemical composition comprising of primary Fe oxide with secondary Zr oxide. The formation of those nanoparticles is likely to originate from the H₂/H₂O-mediated redox process.



Fig. S4 Morphology of Fe-based redox materials (a) pre-test; (b) post-test; (c) EDS analysis; (d) a close look of the morphology of nanoparticles

Table S2 shows the microstructural parameters measured by mercury porosimetry method of Fe-based redox material loaded in the RCU. After the test, the average pore diameter was significantly increased, along with a slight increase in the porosity. These results indicate that no obvious sintering has occurred after a 2-week test.

Table S2 Microstructural parameters of Fe-based redox materials loaded in the

RCU measured from mercury porosimetry

| | Pre-test | Post-test |
|---------------------------|----------|-----------|
| Average Pore diameter, µm | 0.692 | 2.244 |
| Porosity, % | 71 | 76 |

XRD examination of Fe-based redox materials

Fig. S5 shows the phase evolution before and after a 2-week test. Before test, Fig.S5(a) shows contains two phases: Fe_2O_3 and ZrO_2 , present in the redox material. After the test, Fig.5(b) shows that the redox materials protected in a 5%H₂-N₂ during shutdown only consists of Fe and ZrO_2 . Based on these XRD results, it is safe to say that ZrO_2 is a stable and inactive support for the Fe-FeO redox system. The presence of ZrO_2 helped prevent the coarsening of Fe particles during this prolonged battery operation.



Fig. S5 XRD analysis of a Fe-based redox material (a) pre-test; (b) post-test. Sample was protected in a 5%H₂-N₂ during shutdown.

References

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