Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting Information

Demonstration of 10+ Hour Energy Storage with $\phi 1''$ Laboratory Size Solid Oxide Iron-Air batteries

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Thermodynamic aspects of SOIAB

We here show how to calculate thermodynamic properties of Fe-O system. At 550 °C, the equilibrium between Fe and O_2 in SOIAB is given by [1]

$$3Fe(s) + 2O_2(g) \Leftrightarrow Fe_3O_4(s) \tag{S1}$$

The theoretical Nernst potential (E_N) related to this reaction is determined by:

$$E_N = E^o - \frac{RT}{nF} \ln\left(\frac{1}{[pO_2]^2}\right) \tag{S2}$$

where $E^o = -\frac{\Delta G^0}{nF}$, which refers to the EMF under the standard state; ΔG^0 is the standard Gibbs free energy change of Fe-Fe_3O_4 at 550 °C; R is the universal gas constant, 8.314 J mol^{-1} K^{-1}; T is the temperature in kelvins; n is the number of electrons transferred in the reaction per mole metal, $n = 8$ for this case; and F is the Faraday constant, 96485 C mol^{-1}; pO_2 is the partial pressure of oxygen, 0.21 atm in air.

The theoretical specific energy (SE*, based on the mass of iron element, Wh kg^{-1}) can be calculated by:

$$SE^{*}\ \left(Wh\,kg^{-1}\right) = \frac{Q^{*} \times E_N}{m_{Fe}(kg)} = \frac{nF \times E_N}{3600\ \times M_{Fe} \times 0.001} \tag{S3}$$

where $Q^{*} = n \times F = I \times t(seconds)$, which refers to the total theoretical charge per mole of Fe; $M_{Fe}$is the molar mass of Fe in g mol^{-1}.

The theoretical specific charge capacity (Q*, based on the mass of Fe, Ah kg^{-1}) can be obtained by:

$$Q^{*}\ \left(Ah\,kg^{-1}\right) = \frac{SE^{*}}{E_N} \tag{S4}$$

The practical specific energy (PSE, or denoted as DSE and CSE in the main text) is determined by the following:

$$PSE\ \left(Wh\,Kg^{-1}\right) = \frac{\int_{t_1}^{t_2} (I \times V)dt}{m_{Fe}(kg)} \tag{S5}$$

where, t_1 and t_2 refers to the duration of charging or discharging, respectively; I is the applied current; V is the actual measured potential. Thus, the round trip efficient (RTE, %) can be calculated by:

$$RTE = \frac{SE_d}{SE_c} = \frac{\int_{t_1}^{t_2} (I_d \times V_d)dt}{\int_{t_1}^{t_2} (I_c \times V_c)dt}\quad 100\% \tag{S6}$$

The subscripts “c and “d” refer to “charge” and “discharge”, respectively.

The C-rate, describing how fast a battery charges and discharges, can be expressed by the applied current. For example, a 1C battery needs one hour to charge or discharge its full capacity (U_{Fe}=100%), while a 0.5C battery requires two hours:

$$I_{@1c} = \frac{nF}{3600\ seconds} \text{ and } I_{@0.5c} = \frac{nF}{7200\ seconds} \tag{S7}$$

Since the energy capacity of this system depends on the metal/metal oxide redox couple, utilization of metal (U_{Fe}, %) is a crucial parameter for SOIAB. They are defined by:

$$t_{Fe}^{*} = \frac{Q_{Fe}^{*}}{I_a} \tag{S8}$$

$$U_{Fe} = \frac{Q_{Fe}}{Q_{Fe}^{*}} = \frac{t_{Fe}}{t_{Fe}^{*}} \tag{S9}$$

where t_{Fe}^{*} is the theoretical full discharge or charge time; Q_{Fe}^{*} is the total theoretical charge capacity per mole Fe; Q_{Fe} and t_{Fe} are the measured charge capacity and actual discharge/charge time (seconds).

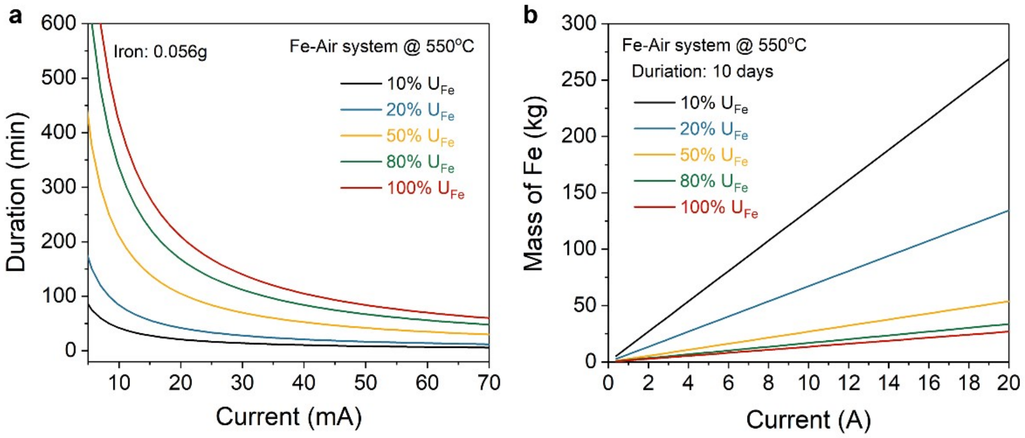


Figure S1. Current-U_{Fe}-duration relationship. (a) Discharge/charge duration with 0.056 g Fe (used in this study) vs. j and U_{Fe}; (b) the mass of Fe for 10 days storage at different *j* and U_{Fe}.

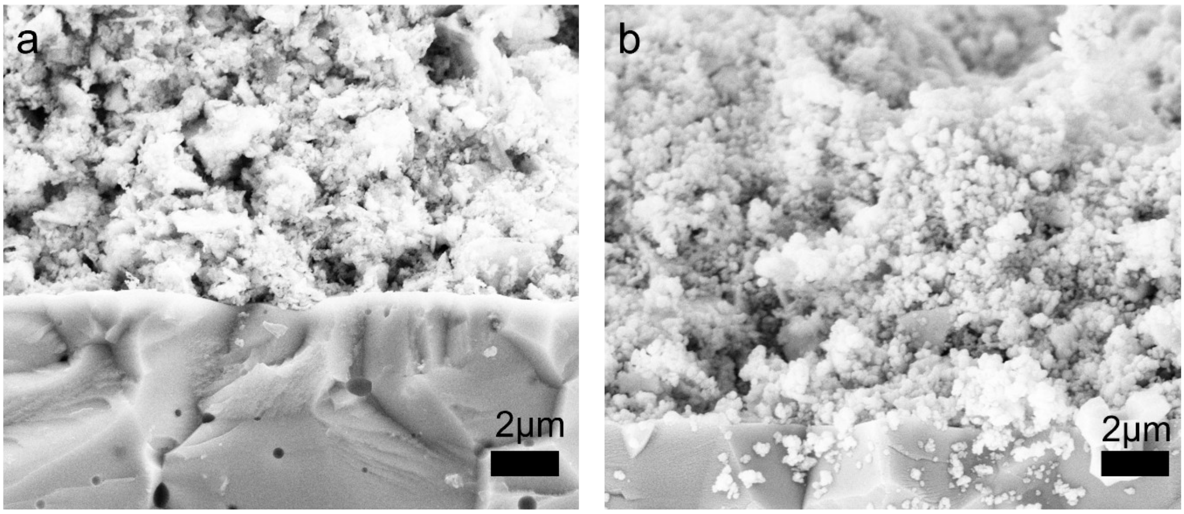


Figure S2 SEM images of LSM/BYC OE before (a) and after (b) 250h testing at 0.2C and 550^{o}C.

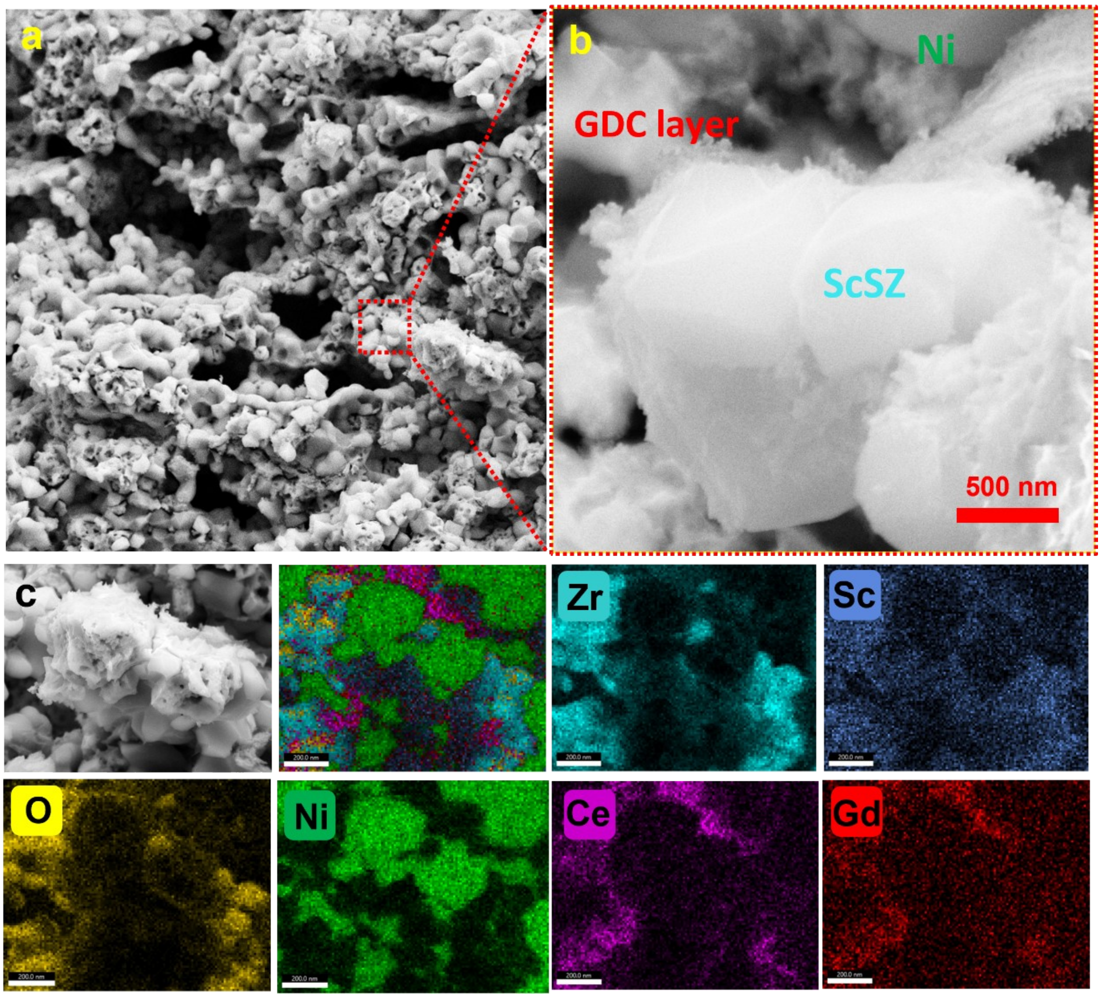


Figure S3. (a and b) SEM images of 4 wt% GDC infiltrated HE after reduction; (c) corresponded elemental mapping.

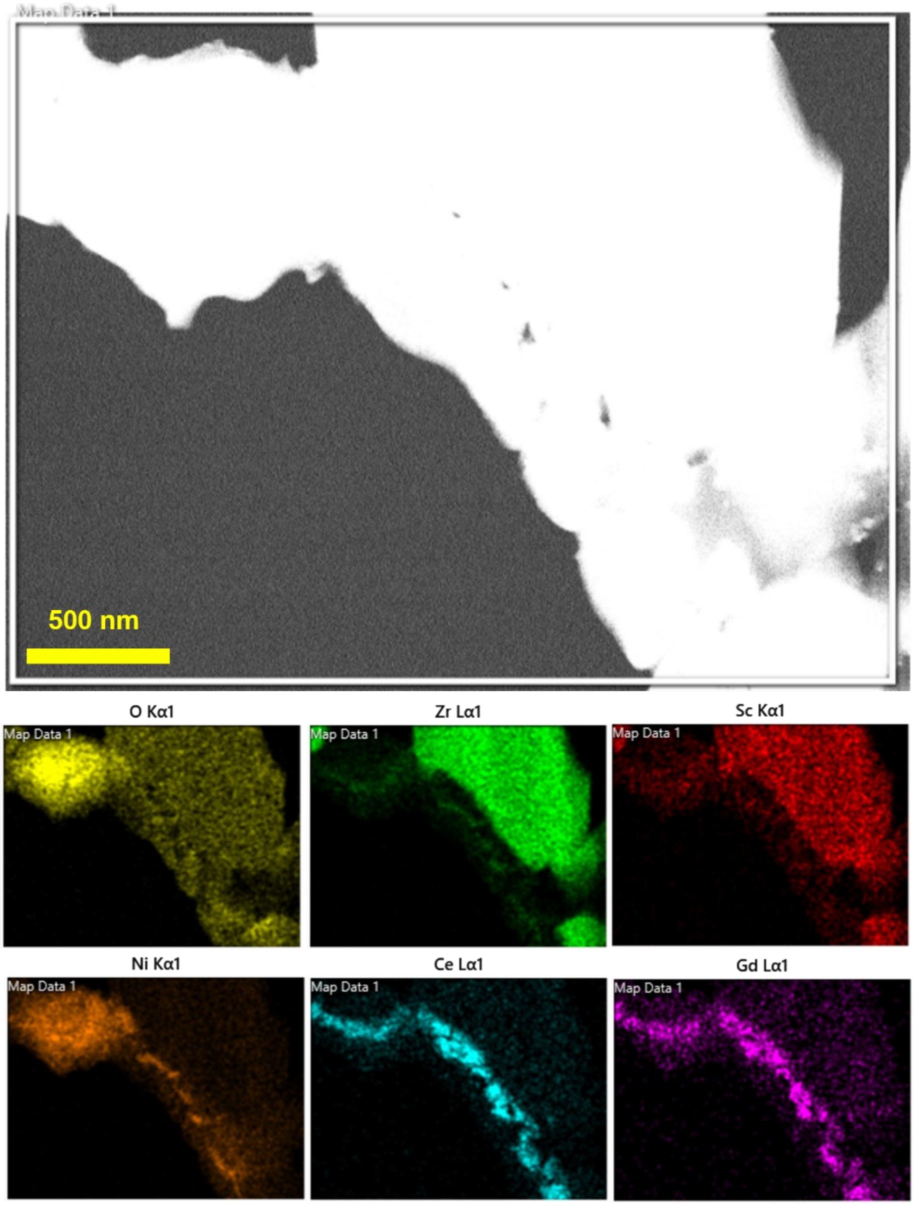
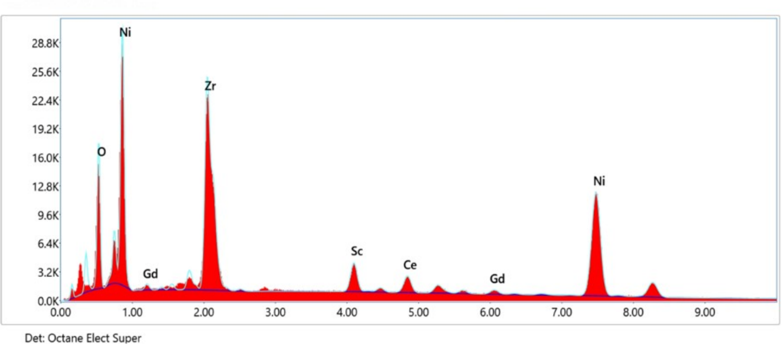
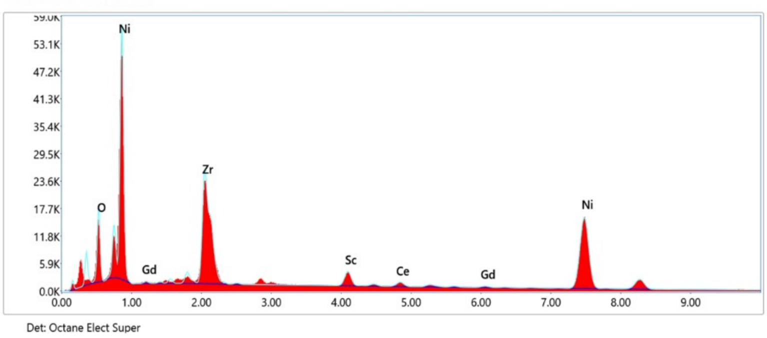


Figure S4. TEM image and the corresponding elemental mapping of 4 wt% GDC infiltrated HE after reduction.



Element	Weight %	Atomic %
O K	10.58	33.63
ScK	3.60	4.08
NiK	53.04	45.97
ZrL	23.25	12.96
CeL	7.25	2.63
GdL	2.28	0.74

Figure S5. EDS spectrum and corresponding elemental contents of 4 wt% GDC infiltrated HE.



Element	Weight %	Atomic %
O K	8.65	27.93
ScK	3.01	3.46
NiK	62.35	54.87
ZrL	21.38	12.10
CeL	3.20	1.18
GdL	1.41	0.46

Figure S6. EDS spectrum and the corresponding elemental distributions of 2 wt% GDC infiltration HE.

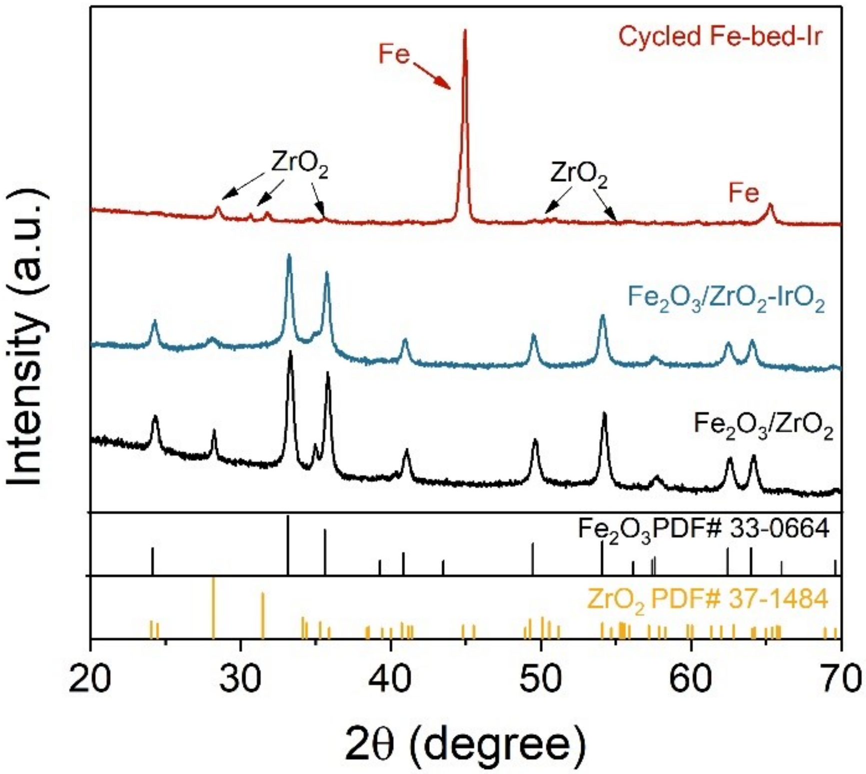


Figure S7. XRD pattern of as-prepared pristine Fe_2O_3/ZrO_2 (bottom) and IrO_2-impregnated Fe_2O_3/ZrO_2 (medium) and corresponding cycled Fe-bed -Ir (top) at U_{Fe}=50% and 0.2C.

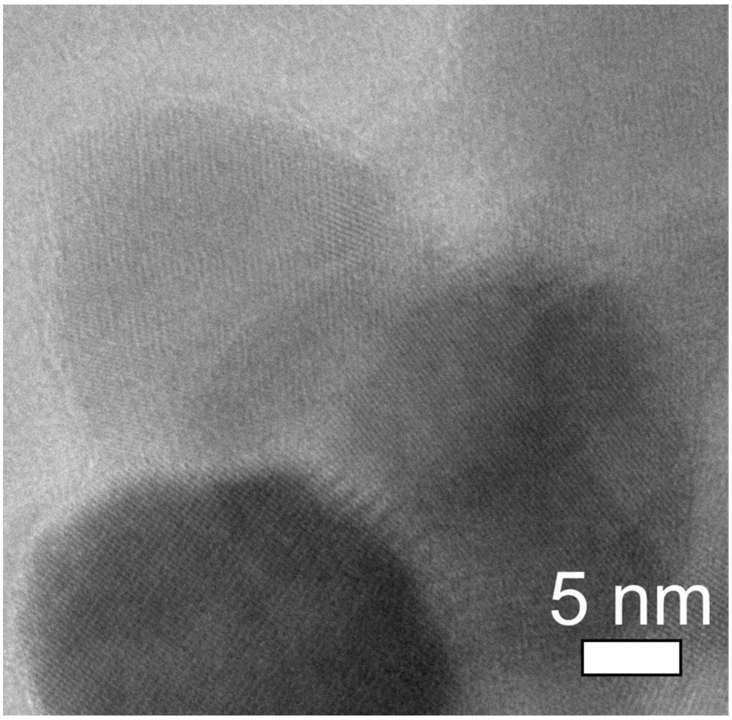


Figure S8. HRTEM image of a fresh Fe_2O_3/ZrO_2 sample.

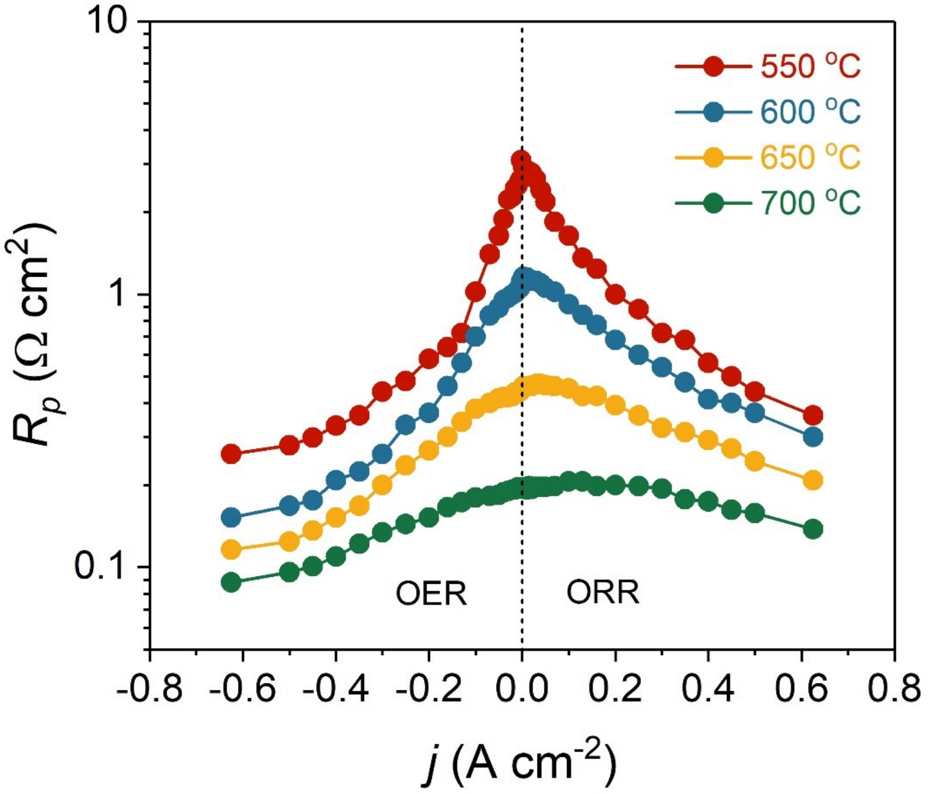


Figure S9. R_p of LSM/BYC OE vs. *j* at different temperatures.

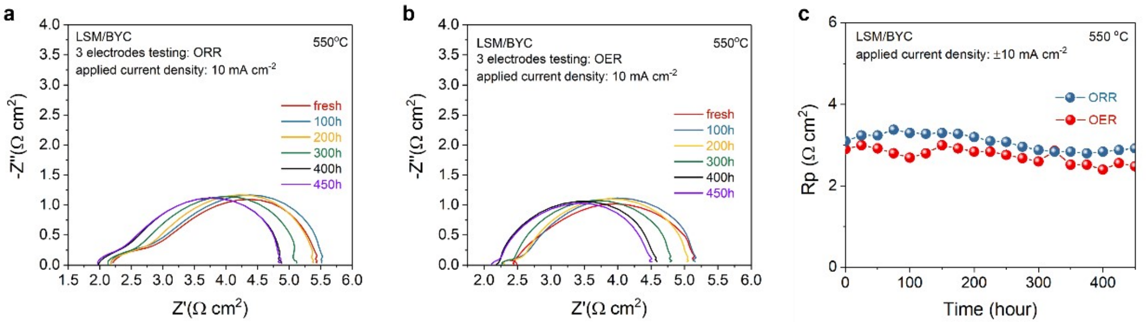


Figure S10. Stability of LSM/BYC OE evaluated by three-electrode symmetric cell under an applied *j*= 10 mA cm^{-2}: (a) EIS spectra vs. time during ORR process; (b) EIS spectra vs. time during OER process; (c) R$_p$ of ORR and OER vs. time.

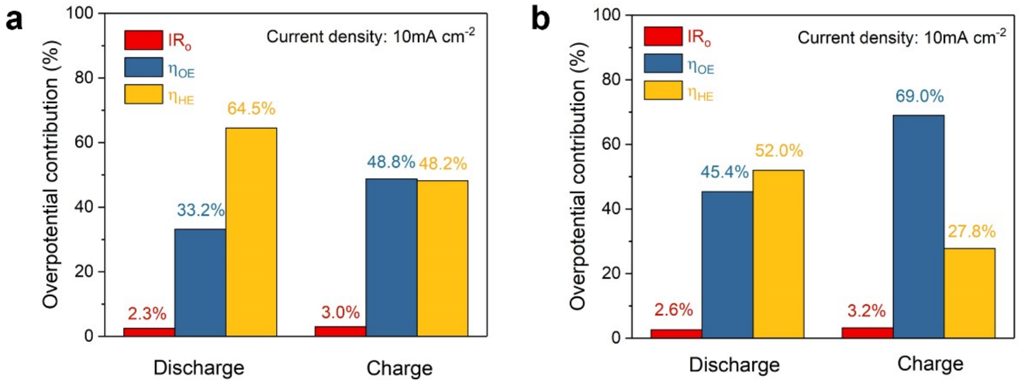


Figure S11. Overpotential contributions during charge and discharge process: (a) 1 wt% GDC infiltrated HE; (b) 4 wt% GDC infiltrated HE.

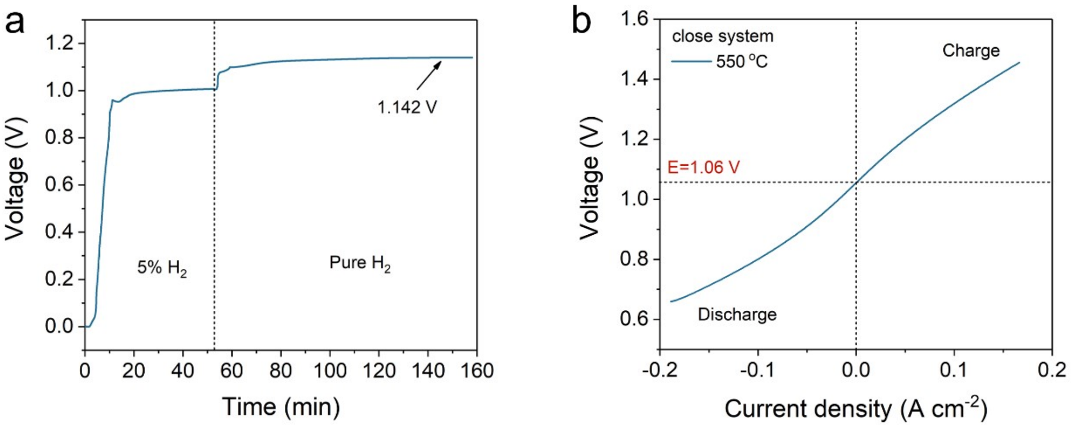


Figure S12. (a) OCV vs. time of RSOC in H_2-3%H_2O for dip-coated cells in open system; (b) *V-j* curve of RSOC in the close system.

The performance of the SOIAB with improved RSOC and Fe_3O_4/ZrO_2-Ir ESU material was tested at 550 °C. Figure S12a shows the variations of OCV of the cell vs. time in H_2-3%H_2O in open system. After full reduction, the cell exhibits a OCV of 1.144 V, which is close to the thermodynamic potential, suggesting a good gas tightness of the system. Then the performance of RSOC was tested in a closed system, where the H_2 inlet and outlet were closed. Figure S12b shows V-*j* curves in both fuel cell and electrolyzer modes in the close system, where the OCV of battery is seen to decrease to ~1.06 V, the thermodynamic equilibrium voltage for Fe-Fe_3O_4 redox couple at 550°C.

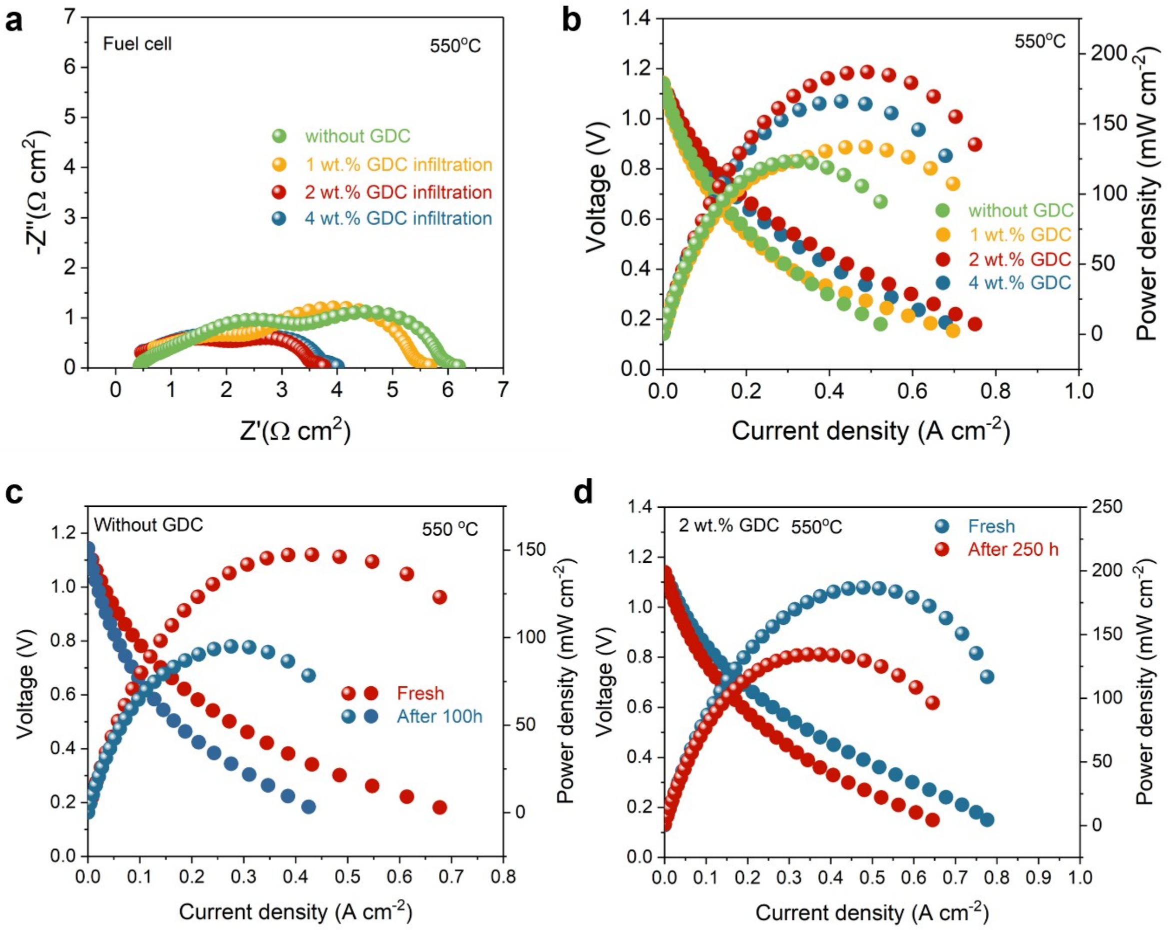


Figure S13. Comparison of cell performance at different GDC loadings: (a) EIS; (b) V-I and P-I curves; (c) performance of 2 wt.% GDC infiltrated cell before and after testing; (d) performance of baseline cell before and after testing.

Figure S13a summarizes the ohmic resistance (R_o) and electrode polarization resistance (R_p) values. The R_o remains a constant for different electrodes, while R_p decreases gradually with the GDC loading, which is attributed to the additional catalytic activity of GDC. The performance was also evaluated in a single cell. The V-*j* curves (Figure S13b) indicates the maximum power density reaches to 200 mA cm^{-2} at 550 ^{o}C for 2 wt% GDC infiltrated cell, which has a significant improvement compared to that of baseline HE cell. However, when the GDC loading increases to 4 wt%, the performance did not show further improvement. This behavior could be attributed to the thicker GDC layer covering more active Ni particles (see

Figure 2). Therefore, 2 wt% is the optimal GDC loading. In addition, after GDC infiltration, the stability of RSOC is also improved as shown in Figure S13c and S13d.

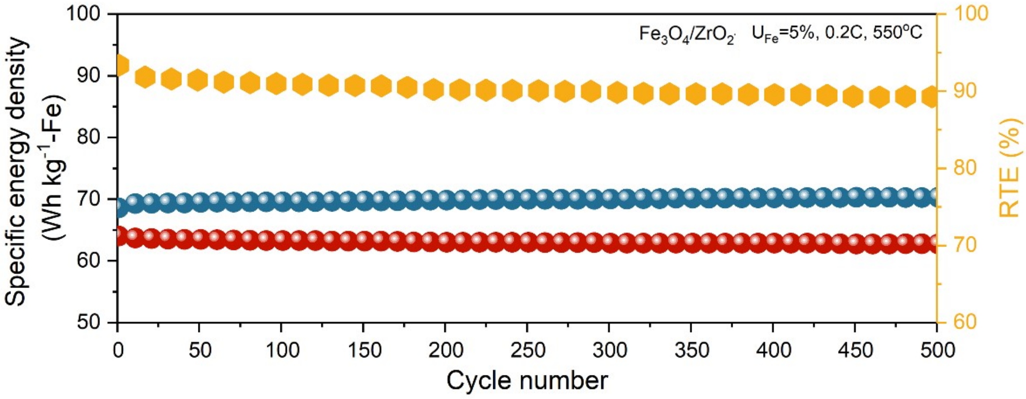


Figure S14. The corresponding SED and RTE of battery with Fe_3O_4/ZrO_2 ESU materials at U_{Fe}=5% and 0.2C.

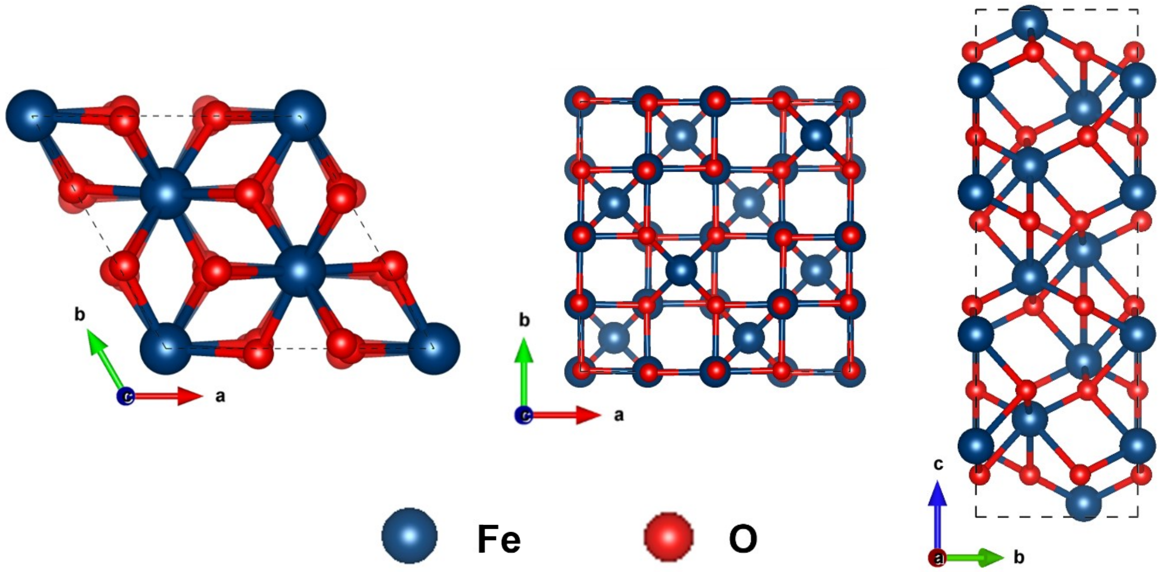


Figure S15. Illustrations of Fe_3O_4 crystal structure in different views.

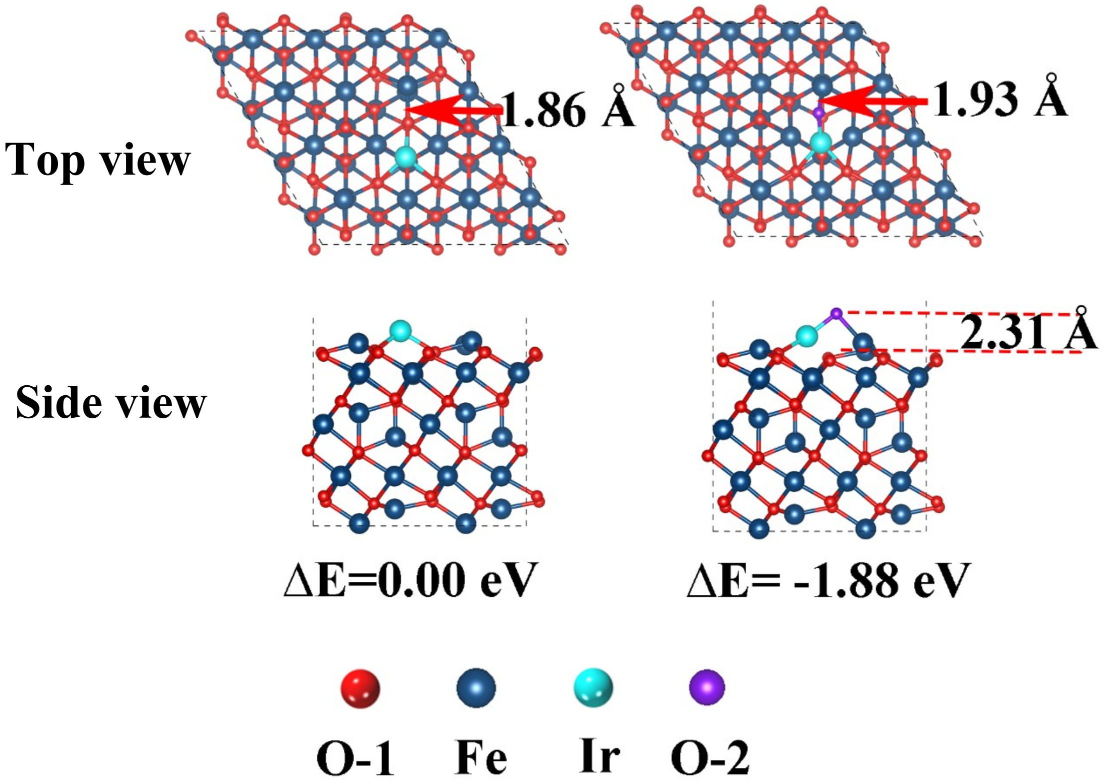


Figure S16. Top view and side view of two Fe_3O_4-Ir (111) surface structures along with the relative energy.

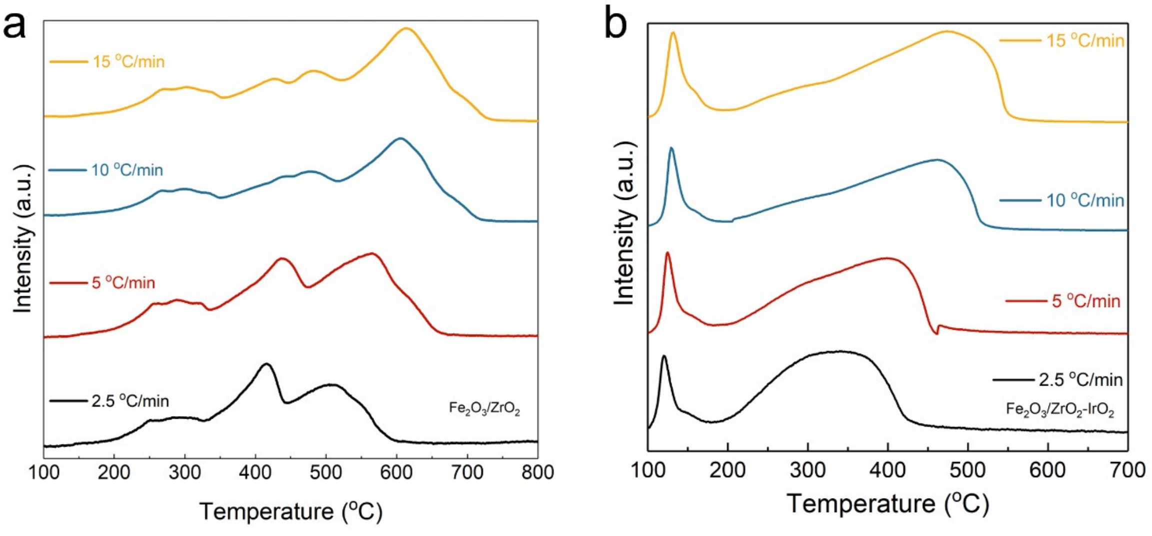


Figure S17. TPR profiles under different ramping rates of 2.5-15 °C/min for (a) fresh Fe_2O_3/ZrO_2; (b) fresh Fe_2O_3/ZrO_2-IrO_2.

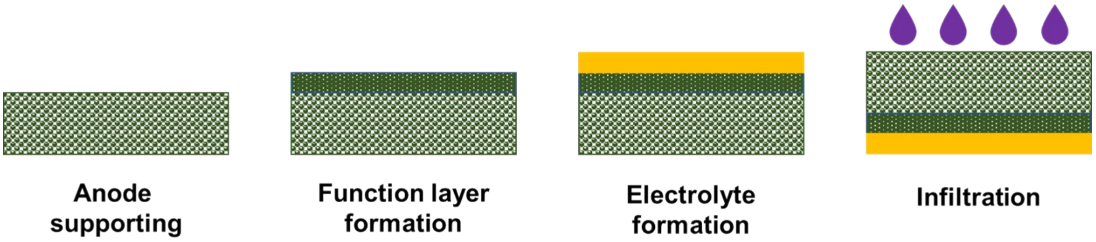


Figure S18. Schematic of HE-supported half-cell fabrication process including GDC infiltration.

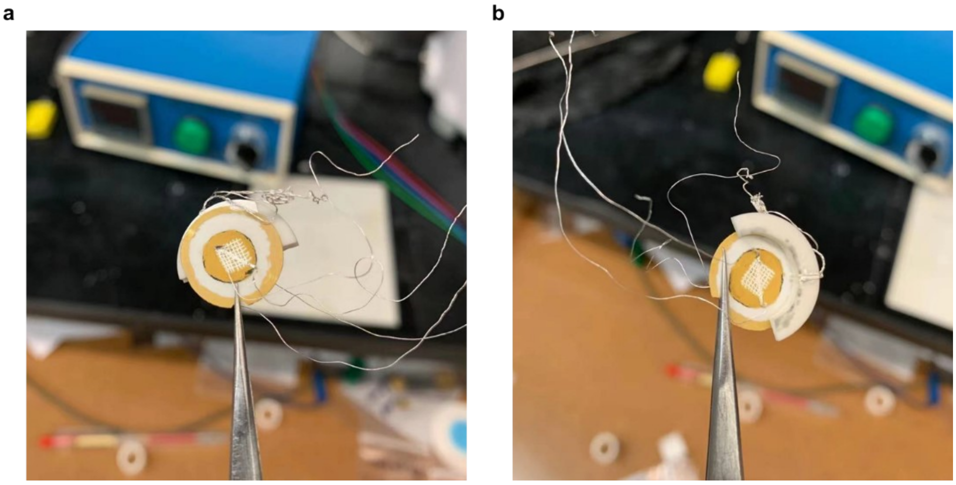
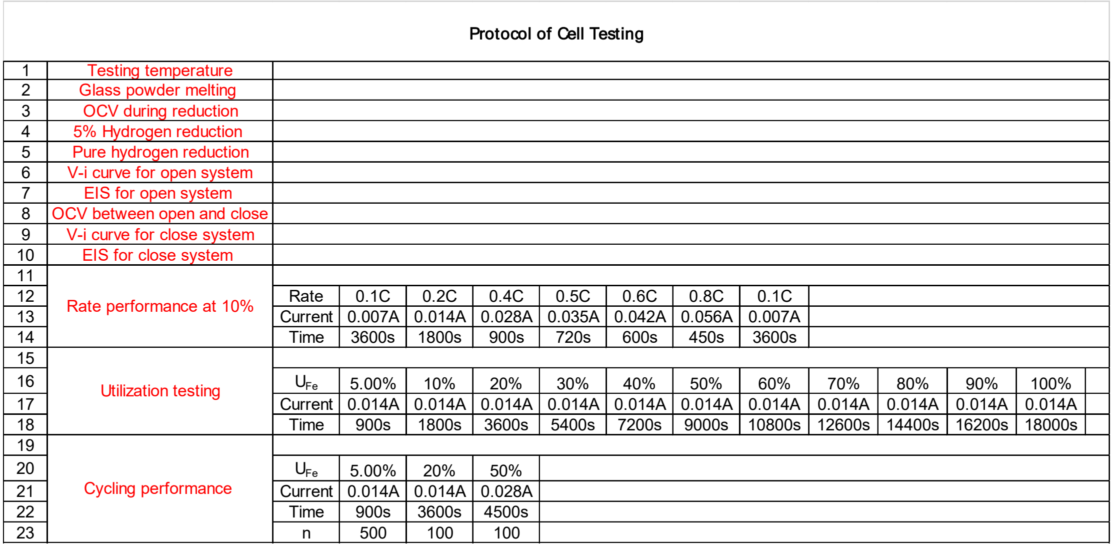


Figure S19. Picture of a three-electrode symmetric cell: (a) front; (b) back. Yellow: gold paste; center: Ag mesh; white: ScSZ electrolyte.

Table S1. Electrochemical testing protocol for SOIAB with 0.001 mol Fe-loading as an example.



Protocol of Cell Testing

1	Testing temperature												
2	Glass powder melting												
3	OCV during reduction												
4	5% Hydrogen reduction												
5	Pure hydrogen reduction												
6	V-i curve for open system												
7	EIS for open system												
8	OCV between open and close												
9	V-i curve for close system												
10	EIS for close system												
11	Rate performance at 10%												
12		Rate	0.1C	0.2C	0.4C	0.5C	0.6C	0.8C	0.1C				
13		Current	0.007A	0.014A	0.028A	0.035A	0.042A	0.056A	0.007A				
14		Time	3600s	1800s	900s	720s	600s	450s	3600s				
15	Utilization testing												
16		U_{Fe}	5.00%	10%	20%	30%	40%	50%	60%	70%	80%	90%	100%
17		Current	0.014A	0.014A	0.014A	0.014A	0.014A	0.014A	0.014A	0.014A	0.014A	0.014A	0.014A
18		Time	900s	1800s	3600s	5400s	7200s	9000s	10800s	12600s	14400s	16200s	18000s
19	Cycling performance												
20		U_{Fe}	5.00%	20%	50%								
21		Current	0.014A	0.014A	0.028A								
22		Time	900s	3600s	4500s								
23		n	500	100	100								

References

[1]. Zhang, C.; Ji, C.; Wang, W.; Schmidt, D.; Jin, X.; Lemmon, J. P.; Huang, K., *Energy Environ. Sci.* **2016,** *9* (12), 3746-3753.