Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting information

for

Ultrafine rhodium selenides enable efficient oxygen reduction reaction catalysis

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Experimental section

Fundamental characterization:

Titan G260-300 supplied with TEM pictures, HR-TEM, SAED patterns and EDS mappings of the samples. XPS spectra were performed using Escalab 250Xi (Thermo Scientific). Bruker AXS D8-Focus was collected to observe the XRD spectra in the range from 10 °to 90 ° with a scan rate of 2° min^{-1}. The data of TG were acquired by STA 409 PC. The TriStar II 3020 (Micromeritics Instrument Corporation, USA) was used to analyze the BET surface areas in an atmosphere of nitrogen. O_2 temperature-programmed desorption (O_2-TPD) experiments were performed on AutoChem1 II 2920. Before the test, the samples were under a flow of 20 % O_2/N_2 mixture (20 ml min^{-1}) for 2 hours in order to absorb O_2. Then the gas was switched to He (20 mL min^{-1}) at room temperature for 1 hour. At last the samples were heated up to 400 °C at the heating rate of 10 °C min^{-1}.

Oxygen reduction reaction:

The oxygen reduction reaction performance of the electrocatalysts were measured in 1 M KOH electrolyte which was based on a three-electrode cell applying CHI. The polished glassy carbon electrode (GCE, D=4 mm) as working electrode which was prepared as follow: 2.0 mg electrocatalyst was dispersed in 0.8 mL isopropanol, 0.18 mL deionized water and 20 μL Nafion (5 wt%). Then a homogeneous solution was formed after ultrasound 1 hour. The electrocatalyst ink was dropped onto the GCE and dried naturally at room

temperature to form a uniform electrocatalyst film (catalyst loading: 0.285 $g \cdot cm^{-2}$).

Firstly, bubble the electrolyte with oxygen about 30 minutes to insure that O_2 was saturated. The polarization curves were scanned at a rate of 5 mV s^{-1} with a rotating speed at 400, 600, 800, 1200, 1600, 2400 rpm, respectively. The durability was demonstrated by CV cycles between -0.3 to -0.6 V vs. RHE at a rate of 100 mV s^{-1}. The amperometric (i-t) measurement was testified \ for 10 h. In addition, 1 M methanol was added to test the methanol tolerance of the catalyst.

Zinc-air battery test:

Made the ink in the same way and sprayed it on a 1 cm^2 carbon paper electrode as a cathode (catalyst mass loading: 1 mg cm^{-2}). And a polished zinc sheet as an anode. The electrolyte of homemade Zinc-air battery included 6 mol L^{-1} KOH and 0.2 mol L^{-1} Zinc acetate. The performance of the battery was assessed. The constant current discharge was tested at constant current density of 5, 10, 20 mA cm^{-2}, respectively. And the specific capacity was measured at constant current density of 5 mA cm^{-2}.

Table S1 Summarized results of Rh/C and Rh3Se4/C from XPS quantitative analysis.

Sample	C 1s (wt%)	Rh 3d (wt%)	Rh^0:Rh^{x+}	Se 3d (wt%)
Rh/C	95.2	4.8	3.8:1	0
Rh_3Se_4/C	93.4	4.5	3.6:1	2.1

Table S2 Comparison of ORR performance of recently reported Rh based electrocatalysts.

Sample	Rh loading (μg cm^{-2})	$E_{1/2}$ (V vs. RHE)	Ref.
Rh_3Se_4/C	14.3	840	this work
$Tl_2Rh_2O_7$	86.1	840	[1]
$Rh_3(C_6O_6)_2$	NA	790	[2]
P-$Bi_2Rh_2O_{6.8}$	85.6	820	[3]
Rh@NPCP	24.6	840	[4]
Rh nanosheets	39.9	879	[5]
Rh–Pd/C	10.0	780	[6]

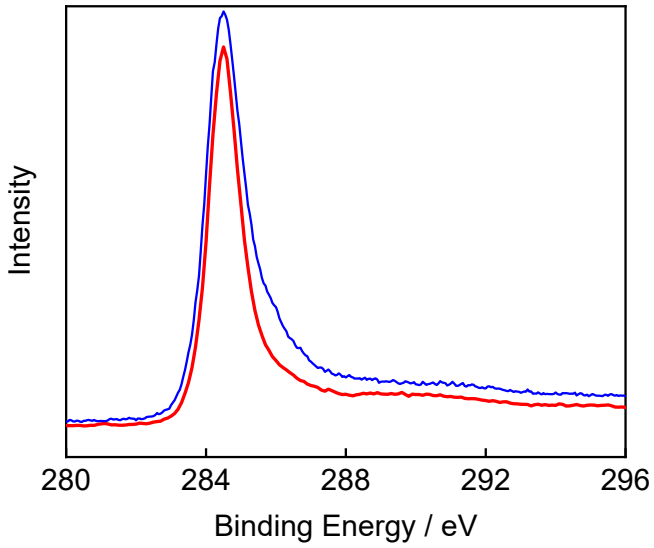

Figure S1 Calibrated C1s peaks of Rh/C and Rh_3Se_4/C electrocatalysts.

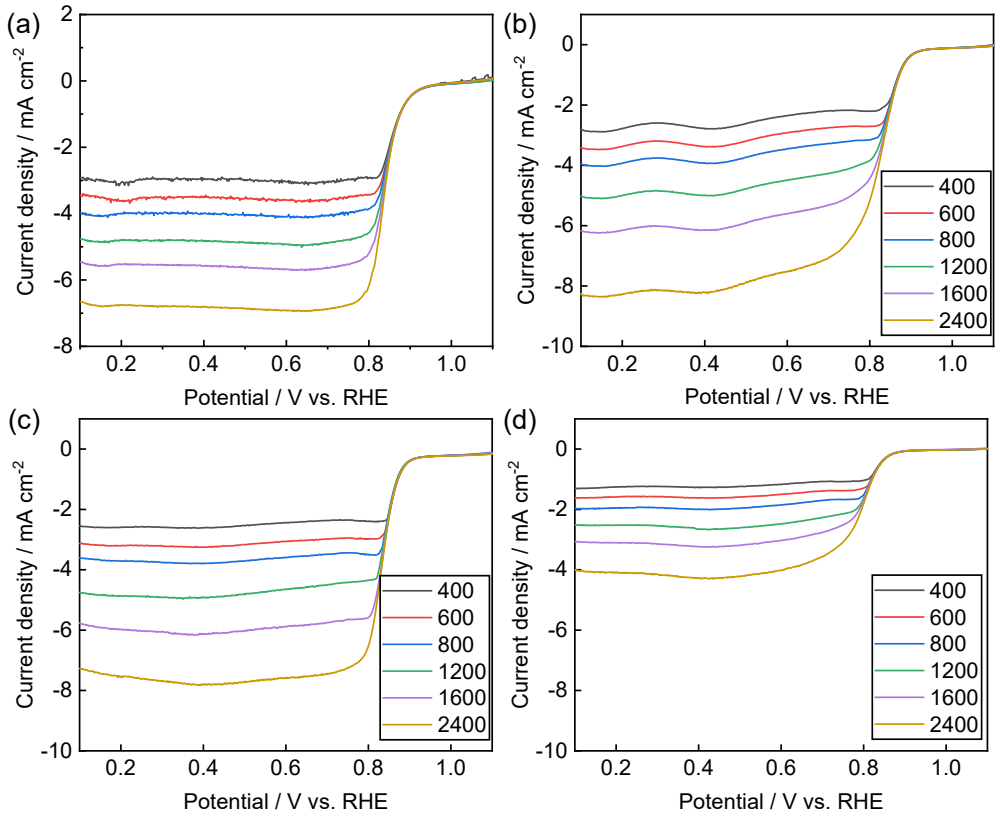

Figure S2 LSV curves of Pt/C (a), Rh/C (b), Rh_3Se_4/C (c) and Se/C (d) electrocatalysts recorded at various rotation speeds.

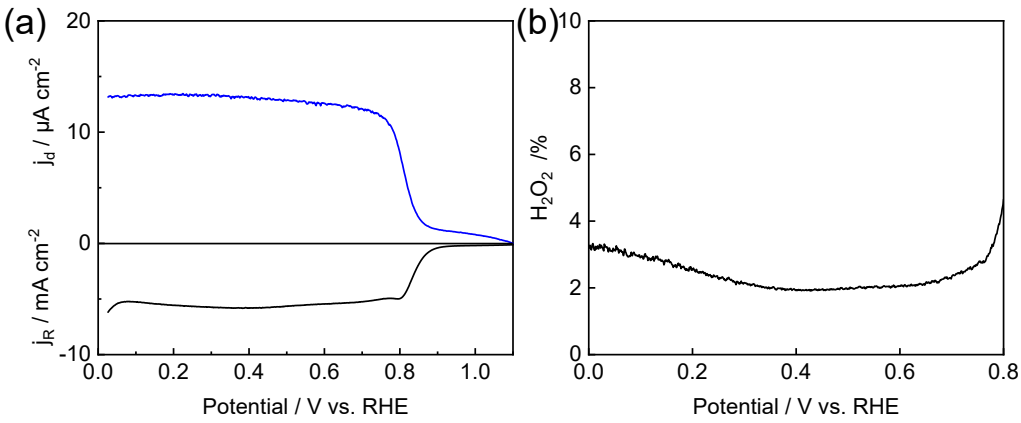

Figure S3 (a) Ring and disc current densities of Rh_3Se_4/C recorded at 1600 rpm. (b) Calculated H_2O_2 generation of Rh_3Se_4/C electrocatalyst.

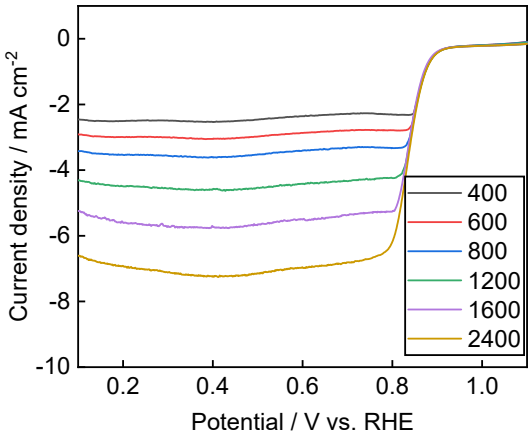

Figure S4 LSV curves of Rh_3Se_4/C electrocatalyst recorded at various rotation speeds.

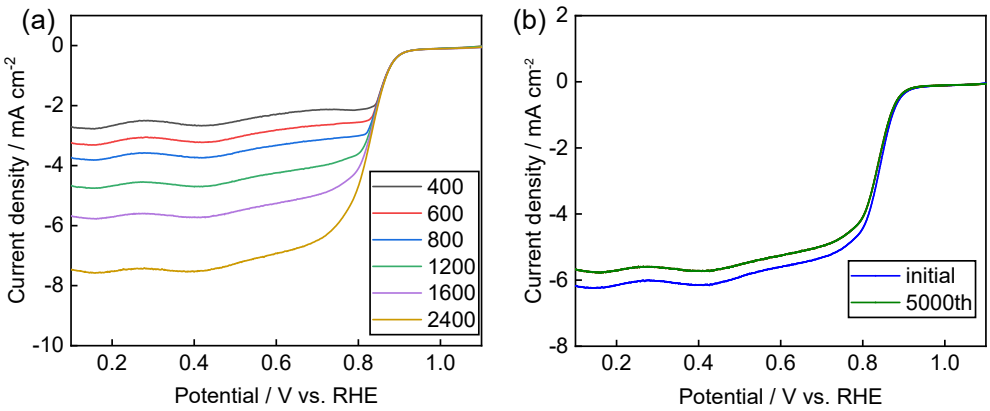

Figure S5 (a) LSV curves of Rh/C electrocatalyst recorded at various rotation speeds after 5000 potential cycles. (b) LSV curves of Rh/C electrocatalyst recorded before and after 5000 potential cycles.

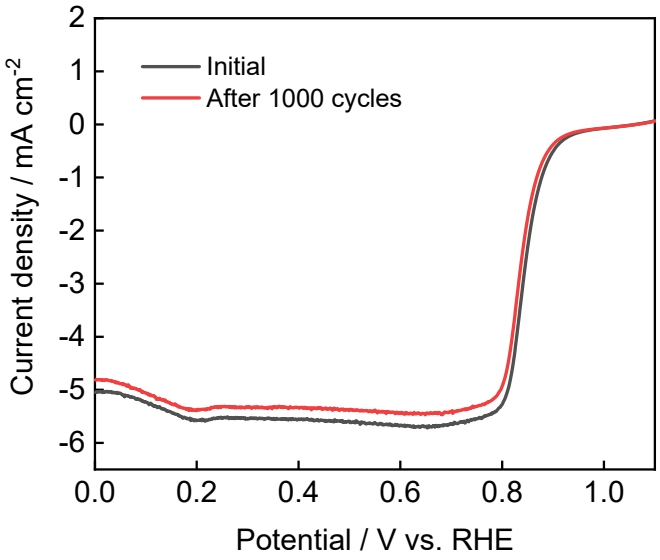

Figure S6 LSV curves of Pt/C electrocatalyst recorded before and after 1000 potential cycles.

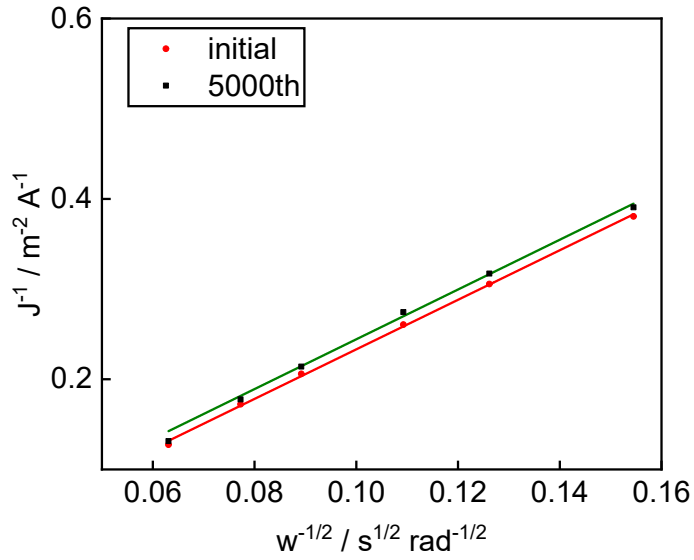

Figure S7 Calculated numbers of electron transferred during ORR before and after 5000 potential cycles.

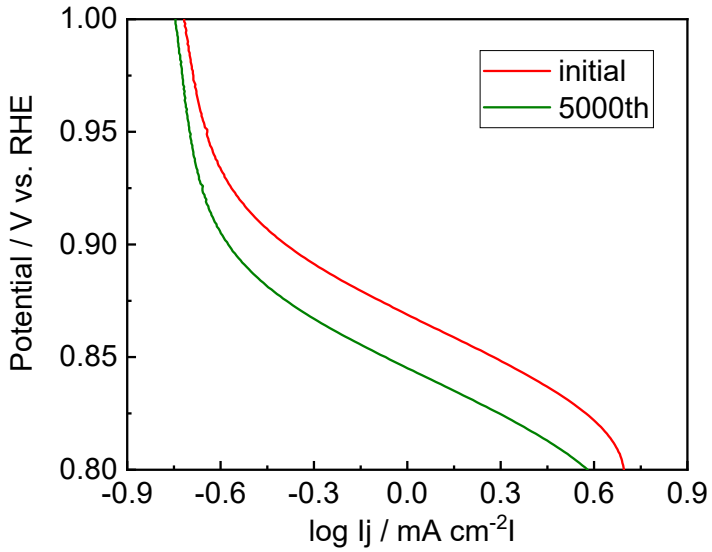

Figure S8 Tafel slopes of Rh_3Se_4/C electrocatalyst before and after 5000 potential cycles.

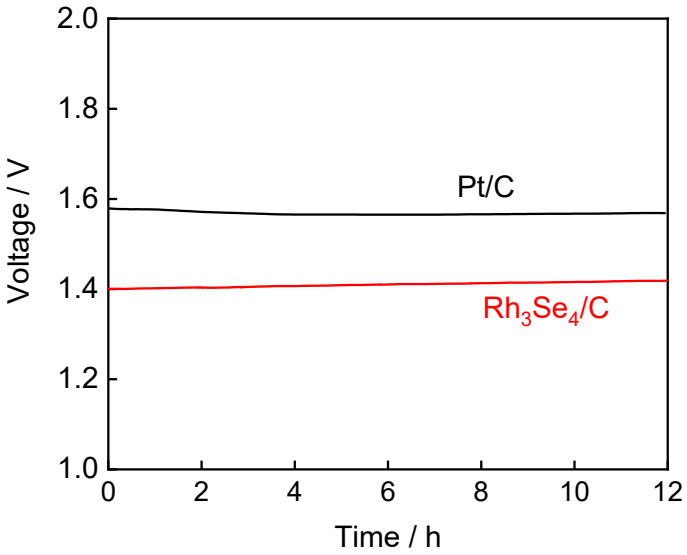

Figure S9 Open circuit voltage (OCV) test of Pt/C and Rh_3Se_4/C assembled zinc air batteries.

References

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