Supporting Information

Unraveling the role of Se defects on Fe_3Se_4 for electrocatalytic oxygen evolution reaction

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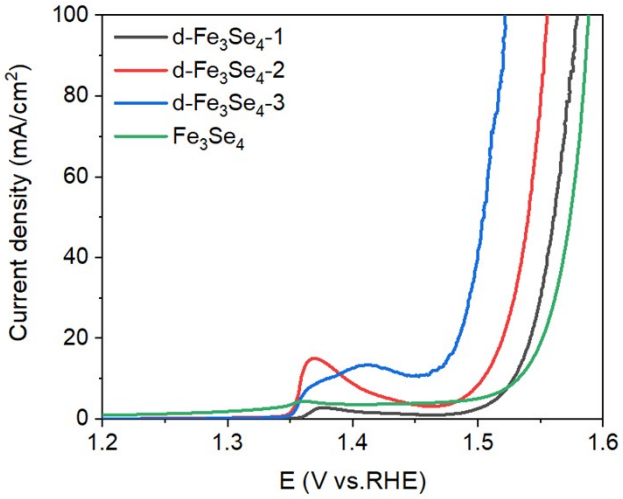

Fig. S1 The results of linear scanning voltammetry tests on d-Fe_3Se_4-1, d-Fe_3Se_4-2, d-Fe_3Se_4-3 and defect-free Fe_3Se_4 with iR correction.

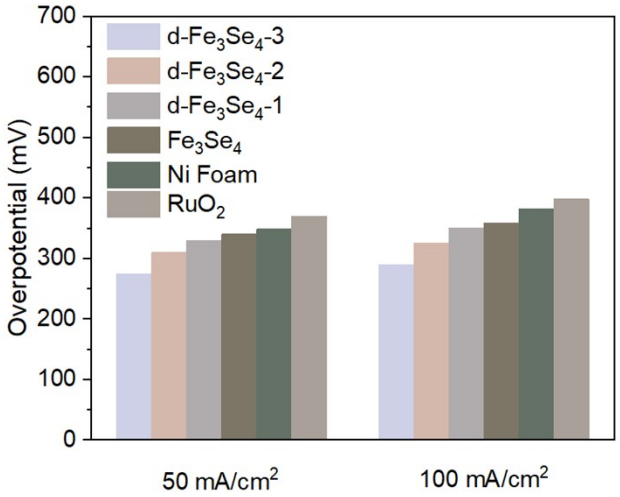

Fig. S2 Comparison of overpotential values for the sample under different current densities.

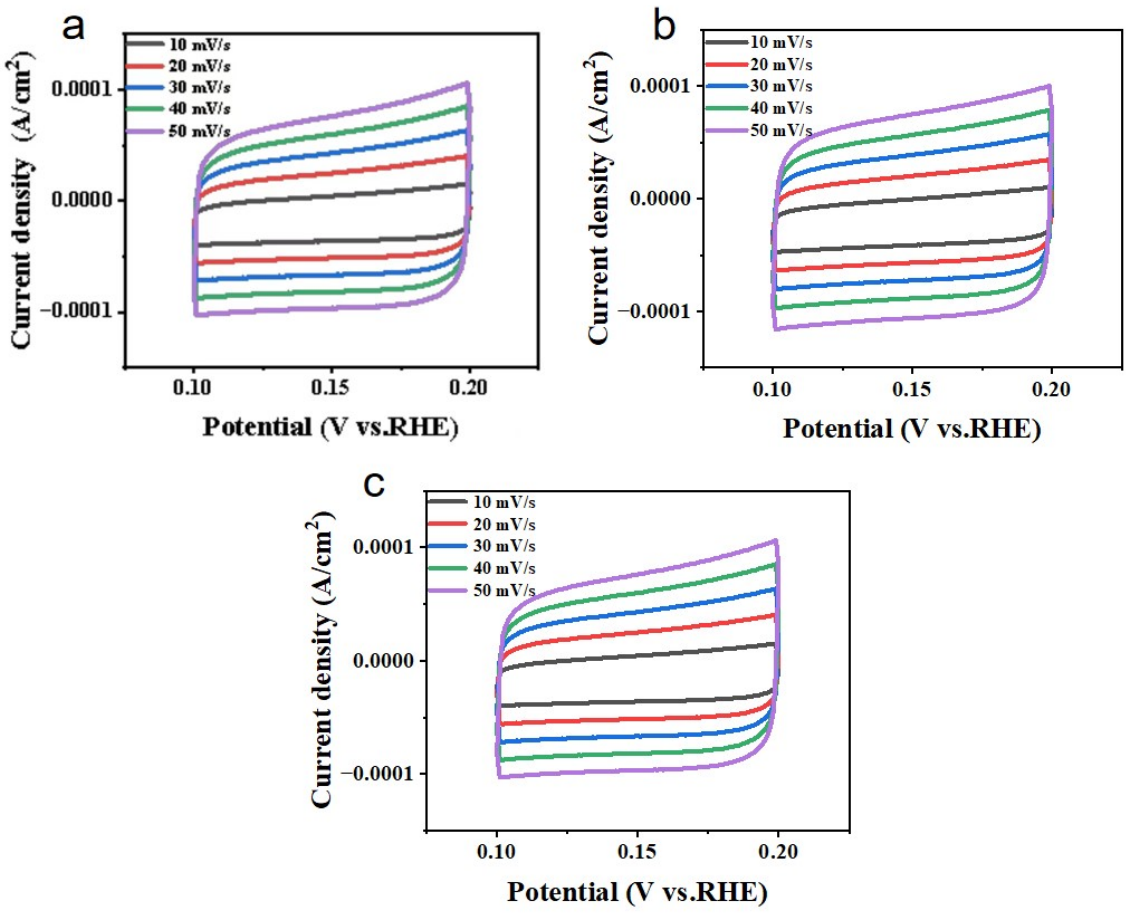

Fig. S3 (a-c) The cyclic voltammograms of d-Fe_3Se_4-3, d-Fe_3Se_4-2 and d-Fe_3Se_4-1 are plotted as a function of scan rate.

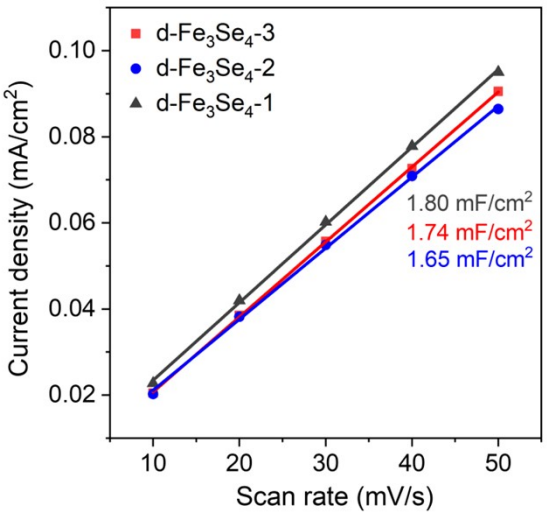

Fig. S4 The double-layer capacitance (C_{dl}) values of d-Fe_3Se_4-1, d-Fe_3Se_4-2 and d-Fe_3Se_4-3.

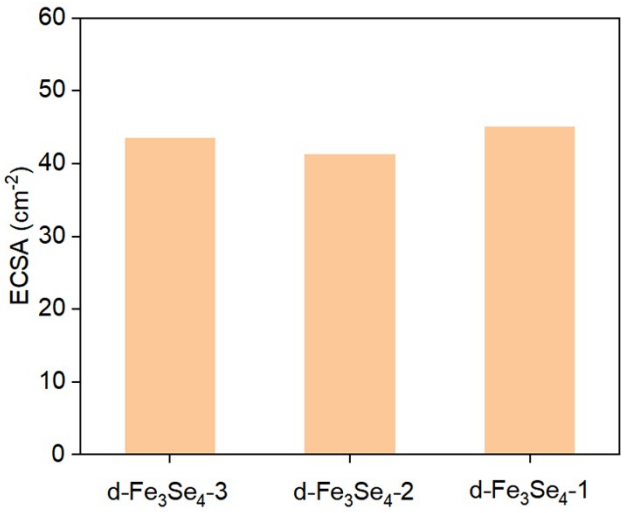

Fig. S5 The electrochemical active specific surface area of d-Fe_3Se_4-3, d-Fe_3Se_4-2 and d-Fe_3Se_4-1.

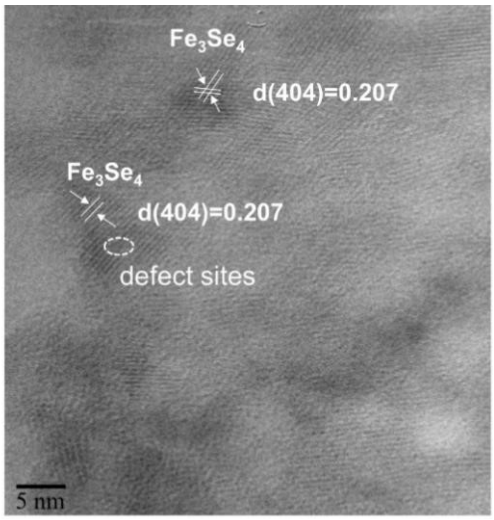

Fig. S6 The HR-TEM image of d-Fe_3Se_4-3 after 100 h stability testing.

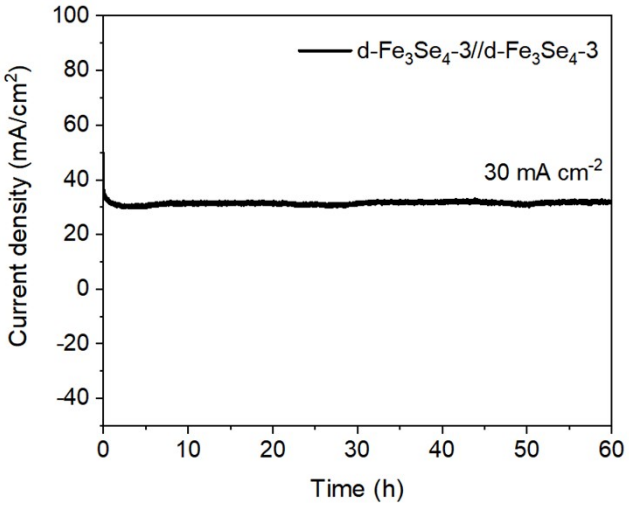

Fig. S7 Chronograph current curve at 30 mA·cm^{-2}.

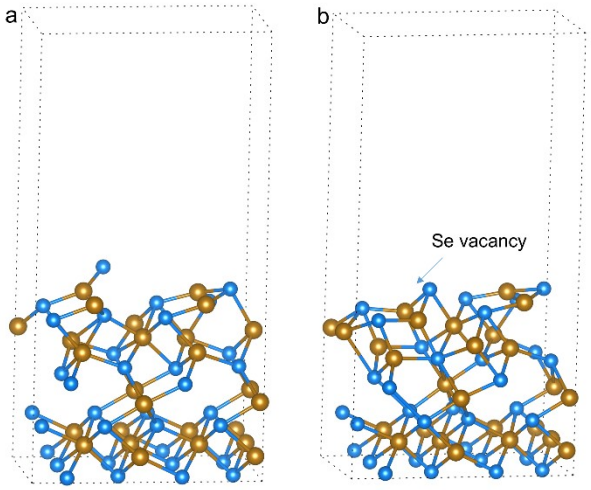

Fig. S8 The calculation models of Fe_3Se_4(100) (a) and Se defected Fe_3Se_4(100) (b).

Table S1 The OER overpotential comparison of various typical electrocatalysts at 50 mA·cm^2.

Catalyst	j/ mA·cm^{-2}	ŋ/mV at the corresponding J	Substrate	Electrolyte	References
d-Fe_3Se_4-3	**50**	**274.8**	**Ni foam**	**1 M KOH**	**This work**
$Ru/NiCoO_{2-x}$	50	470	/	1 M KOH	*Journal of Colloid and Interface Science* **2025**, 686, 509–515
Fe_x-$CoSe_2$/NF	50	275	Ni foam	1 M KOH	*Journal of Alloys and Compounds* **2025**, 1038, 182600
Fe-Co-Se-O-300	50	320	/	1 M KOH	*Materials Chemistry Frontiers* **2025**, 9, 1726
Fe-CoNiCrMo	50	275	Ni foam	1 M KOH	*Catalysts* **2025**, 15, 744
HfNi-WO_3@NF	50	319	Ni foam	1 M KOH	*ACS Applied Energy Materials* **2025**, 8, 6645−6654
$P_{0.79}$-NMO/NF	50	350	Ni foam	1 M KOH	*Journal of Colloid and Interface Science* **2025**, 700, 138556
$FeMnCr_{0.6}$OOH/NF	50	320	Ni foam	1 M KOH	*Chem. Commun.*, **2025**, 61, 5613–5616
Fe-Ni_3P@Ni_8P_3/NF	50	278	Ni foam	1 M KOH	*Colloid Surf. A*, **2025**, 726, 138147
NiCu/$NiMoO_4$/NF	50	300	Ni foam	1 M KOH	*J. Alloys Compd.*, **2025**, 1028, 180701
$Ni_{0.8}Co_{0.2}Ce_{0.1}$/NF	50	275	Ni foam	1 M KOH	*Mater. Today Commun.*, **2025**, 42, 111173
Co – P/Fe_3O_4-3@NF	50	350	Ni foam	1 M KOH	*Int. J. Hydrogen Energy*, **2024**, 62, 803 – 811
PdAg/NiOx	50	310	Ni foam	1 M KOH	*Surf. Interfaces*, **2024**, 44, 103640

Table S2 The relationship between different precursor ratios and vacancy content.

Catalyst	Precursor ratio (Fe:Se)	EPR intensity	The ratio of Se^{-}/Se^{2-}
d-Fe_3Se_4-1	1:1	1	0.4
d-Fe_3Se_4-2	5:1	1.34	0.7
d-Fe_3Se_4-3	10:1	1.74	0.74

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