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

Electronic Supplementary Information (ESI):

New insights into evaluating catalyst activity and stability of oxygen evolution reactions in alkaline media

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Table S1 Physical properties of catalyst samples.

Sample	BET surface area/$m^2\ g^{-1}$	BJH total pore volume/ $cm^3\ g^{-1}$	BJH average pore diameter/nm	Zeta potential*
IrO_2	32.54	0.238	30.2	-25.5
$NiCo_2O_4$	24.67	0.0767	18.0	-22.2

* Zeta potential was measured by using the catalyst ink with Nafion ionomer and catalyst (weight ratio=0.5).

Table S2 Fitted values of each circuit element/parameter at various potentials for IrO_2 catalyst.

Potential	L	R_Ω	R_{ct}	C_1		R_1	C_2	
				$C_{f,1}$	n_1		$C_{f,1}$	n_2
	E^{-7} H cm^2	$\Omega\ cm^2$	$\Omega\ cm^2$	F $cm^{-2}\ s^{n-1}$		$\Omega\ cm^2$	F $cm^{-2}\ s^{n-1}$	
OCP	2.24	0.951	148.37	$1.17E^{-4}$	0.869	-	-	-
1.50 V	2.37	0.953	7.50	$1.46E^{-2}$	0.901	0.0821	0.143	0.626
1.55 V	2.38	0.961	1.75	$1.36E^{-2}$	0.916	0.134	0.562	0.474
1.60 V	2.36	0.962	0.825	$1.30E^{-2}$	0.926	0.100	0.129	0.654
1.65 V	2.35	0.961	0.529	$1.33E^{-2}$	0.908	0.0742	0.0847	0.713

Table S3 Fitted values of each circuit element/parameter at various potentials for $NiCo_2O_4$ catalyst.

Potential	L	R_Ω	R_{ct}	C_1		R_1	C_2	
				$C_{f,1}$	n_1		$C_{f,2}$	n_2
	E^{-8} H cm^2	Ω cm^2	Ω cm^2	F cm^{-2} s^{n-1}		Ω cm^2	F cm^{-2} s^{n-1}	
OCP	12.8	1.00	1182	8.76E^{-5}	0.852	-	-	-
1.50 V	0.384	1.02	33.1	9.79E^{-3}	0.904	1.32	0.237	0.266
1.55 V	6.01	1.03	4.21	8.90E^{-3}	0.904	0.617	0.156	0.324
1.60 V	6.81	1.06	1.57	8.48E^{-3}	0.887	0.315	0.0726	0.421
1.65 V	7.20	1.07	0.954	8.31E^{-3}	0.867	0.215	0.0471	0.480

Table S4. Capacitance and ECSA results obtained from various diagnostic methods.

Method	C* mF	ECSA*@C_s=0.4 F m^{-2} m^2 g^{-1}	ECSA*@C_s=1.3 F m^{-2} m^2 g^{-1}
Single-point current CV	12.55/0.0760	667.6/4.0	205.4/1.2
Integrated CV ($1/C$ vs. $\nu^{1/2}$)	16.03/0.826	852.7/43.9	262.4/13.5
Integrated CV (C vs. $\nu^{-1/2}$)	6.71/0.0409	356.9/2.2	109.8/0.7
EIS at 1.50-1.65 V	(1.77-1.52)/(1.17-0.72)	(94.1-80.9)/(62.2-38.3)	(29.0-24.9)/(19.1-11.8)
EIS at OCP	0.00582/0.00341	0.31/0.18	0.095/0.056

*The values obtained from IrO_2 and $NiCo_2O_4$ are shown in the right and left of "/", respectively.

Reference electrode potential calibration via RHE

Potential calibration of the applied reference electrode (RE) was carried out in H_2-saturated 1 M KOH with a Pt wire as the working electrode. Cyclic voltammetry measurements were conducted at a scan rate of 1 mV s^{-1}. As shown in Fig. S1, the average of two *IR*-free potentials at zero current was calculated to be -0.898 V. Therefore, the reference potential, E_0, used throughout our study was 0.898 V vs. RHE. The WE potential vs. RHE (E_{RHE}) can be calculated as:

$$E_{\mathrm{RHE}} = E_{\mathrm{WE}} + E_0 \qquad \text{* MERGEFORMAT (S1)}$$

where, E_{WE} is the experimental WE potential measured against the RE.

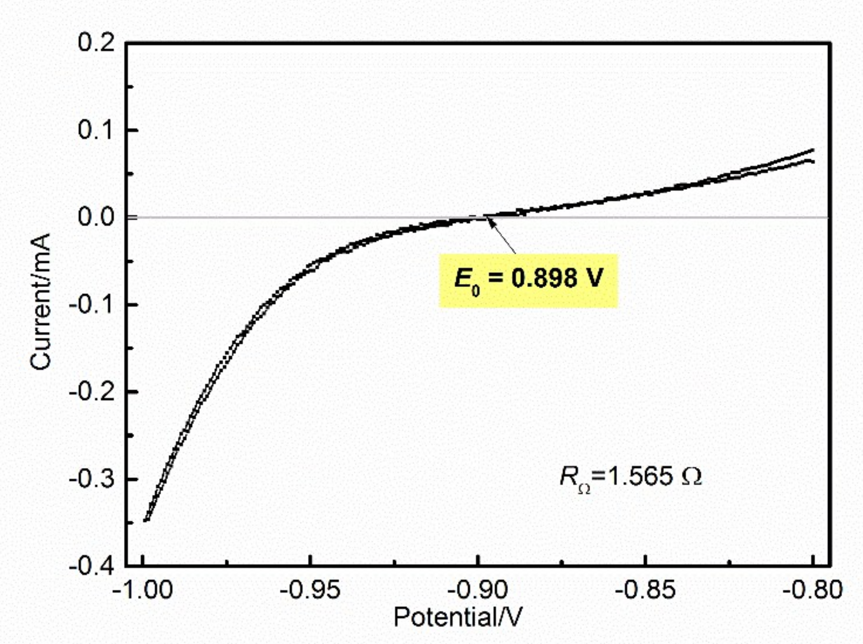

Fig. S1 Potential calibration of Hg/HgO reference electrode (filled in 1 M KOH) vs. RHE in 1 M KOH at room temperature.

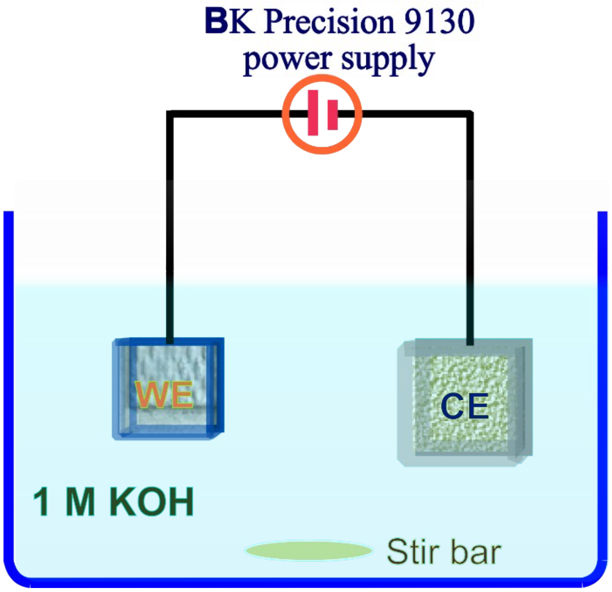

Fig. S2 Experimental setup for catalyst durability test at a constant current density of 10/50 mA cm^{-2} and room temperature in stirred 1 M KOH (200 rpm).

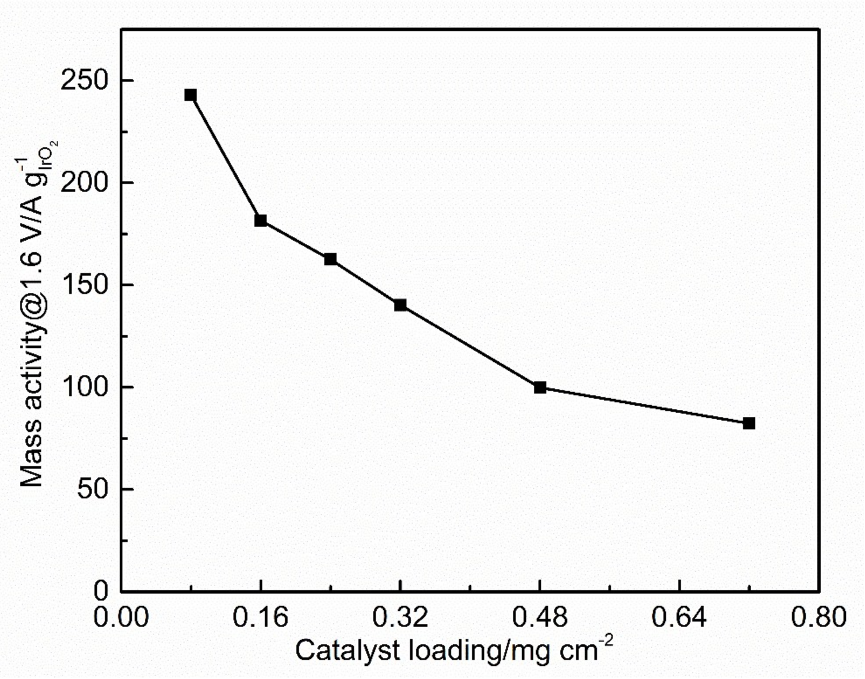

Fig. S3 Mass activity of IrO_2 at 1.6 V as a function of loading.

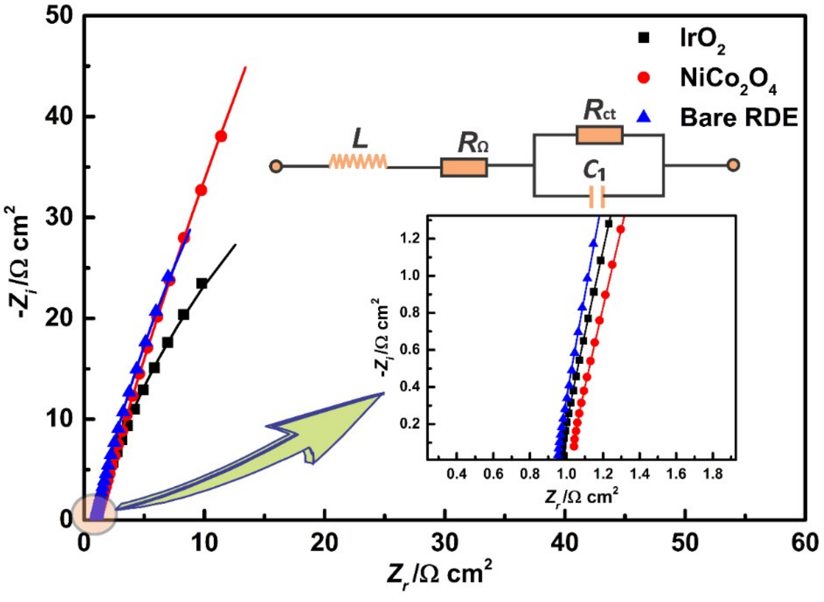

Fig. S4 EIS spectra at open circuit potential. Symbols - raw data; lines – linear fit to the data. The insets are the equivalent circuit fitting (above) and the zoomed in EIS spectra (below) in high-frequency region.

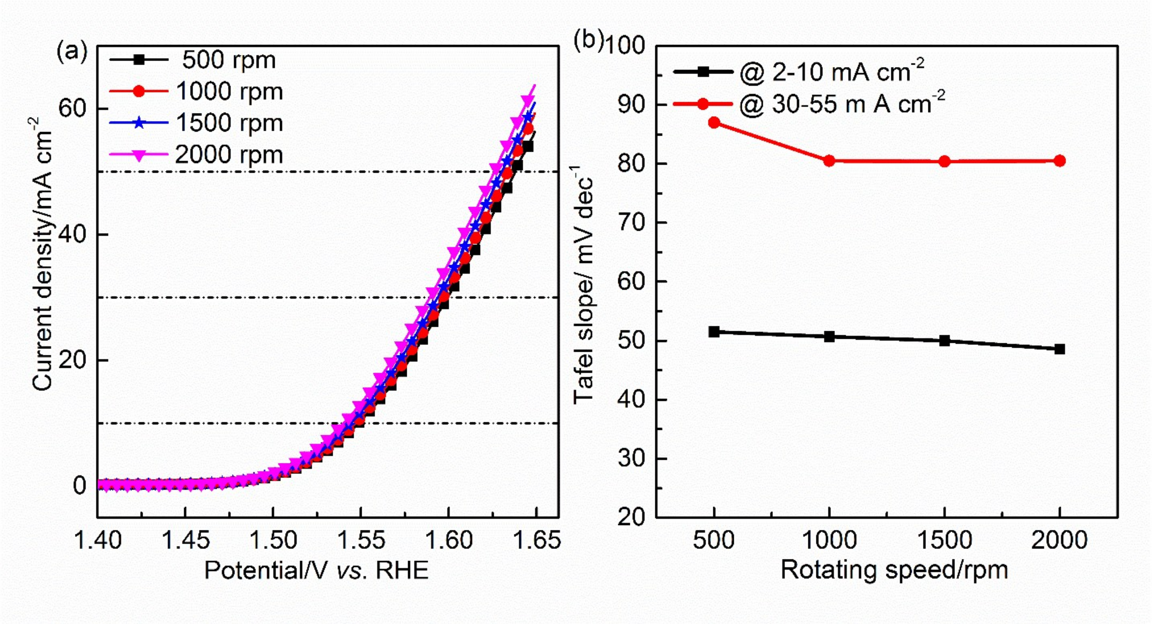

Fig. S5 (a) LSV curves of IrO_2 at a scan rate of 2 mV s^{-1} in 1 M KOH and (b) corresponding Tafel slopes as a function of the rotating speed of the working electrode.

EDL capacitance via integrated CV method

The nature of interfacial capacitance (C) was analyzed using a procedure involves integrating the voltammetric capacitance as a function of scan rate (v) according to:[1]

$$C = \frac{\int_{E_1}^{E_2} |i| \mathrm{d}E}{2v\left(E_2 - E_1\right)} \quad \text{* MERGEFORMAT (S2)}$$

where E_1 and E_2 are the cutoff potentials in CV, i is the instantaneous current. C indicates the amount of OH^- ion flux between the EDL and electrolyte solution. For an infinitely slow scan rate, OH^- is allowed to access all reaction regions, and C approaches total capacitance C_t, which resulted from the entire catalyst active surface. The relationship between C_t and v has been found to be: [1, 2]

$$1/C = 1/C_t + k_1 v^{1/2} \quad \text{* MERGEFORMAT (S3)}$$

The intercept can thus be considered as the reciprocal of C_t which is the sum of the inner (C_i) and outer (C_o) capacitance.

With the increase of v, the highly dynamic process prevents OH^- from diffusing into the less accessible regions, such as micro-pores, cracks, and along grain boundaries.[1] For an infinitely high v, these less accessible regions are excluded, and C acquired from this process can be expressed by C_o as: [1, 2]

$$C = C_o + k_2 v^{-1/2} \quad \text{* MERGEFORMAT (S4)}$$

The intercept, C_o, can be obtained from the plot of C *vs*. $v^{-1/2}$.

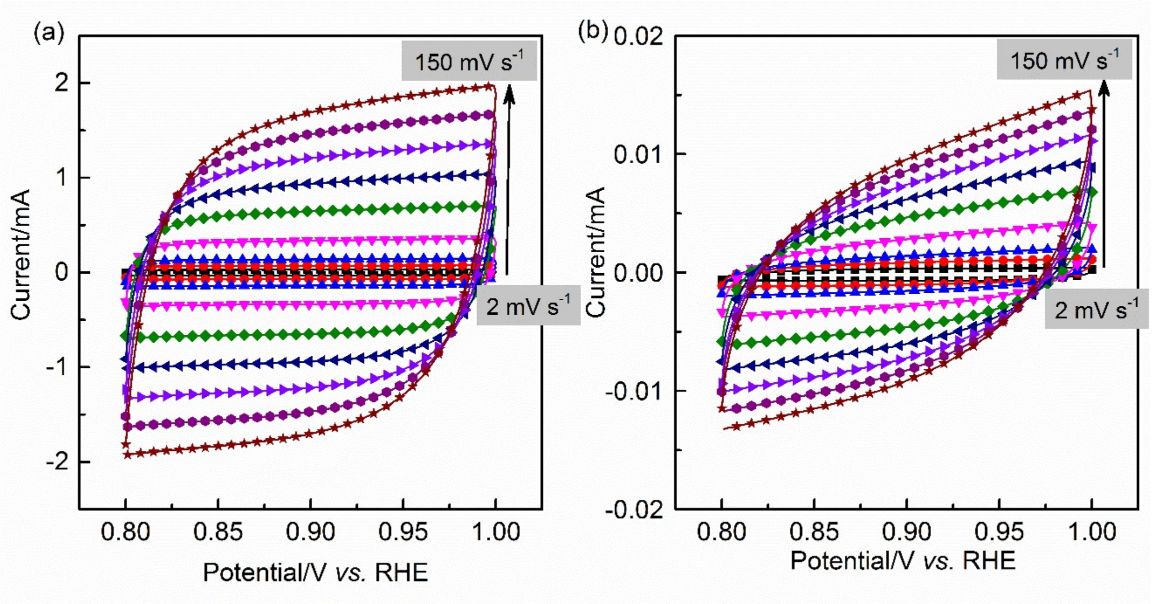

Fig. S6 CV curves of (a) IrO_2 and (b) $NiCo_2O_4$ at various scan rates. The resulted current is corrected by shorting resistance obtained from 2 mV s^{-1}.

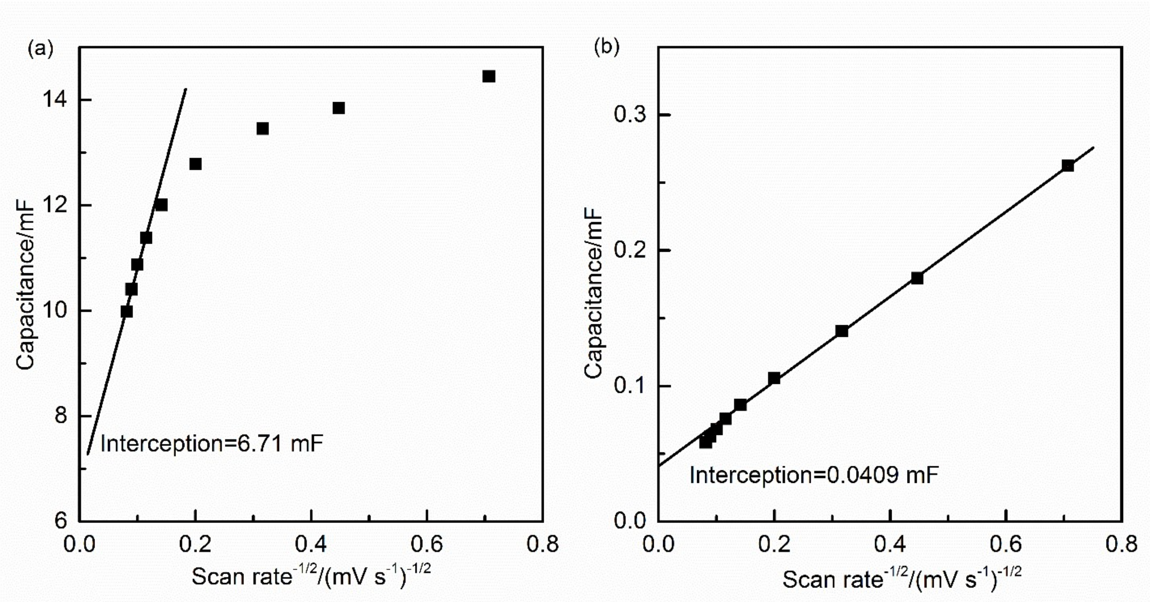

Fig. S7 EDL capacitance of (a) IrO_2 and (b) $NiCo_2O_4$ as a function of square root of CV scan rates. Symbols - raw data; lines – linear fit to the data.

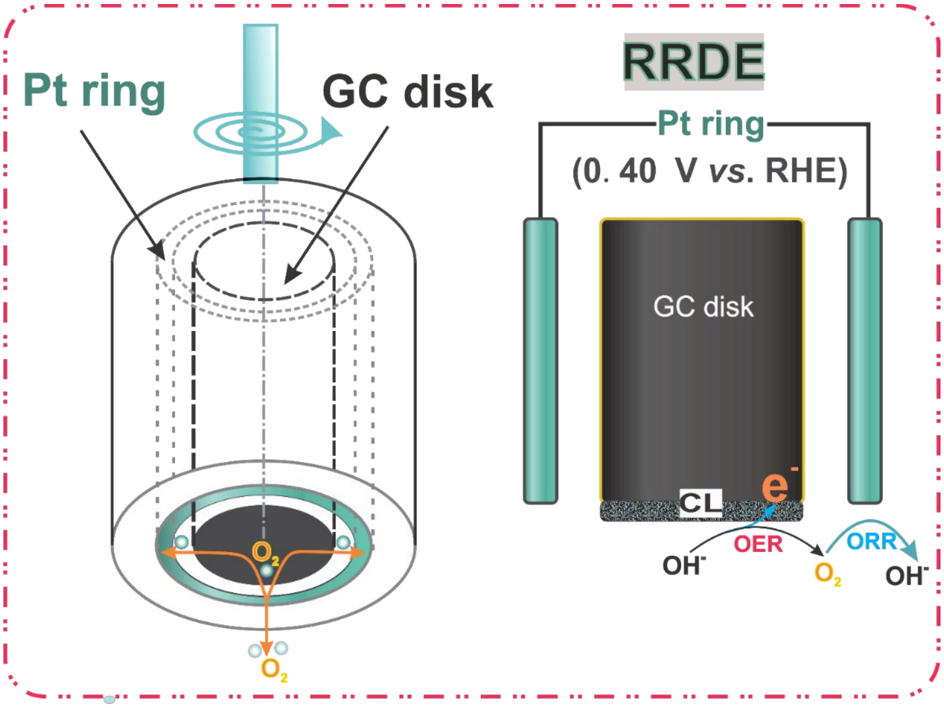

Fig. S8 Schematic illustration of RRDE configuration.

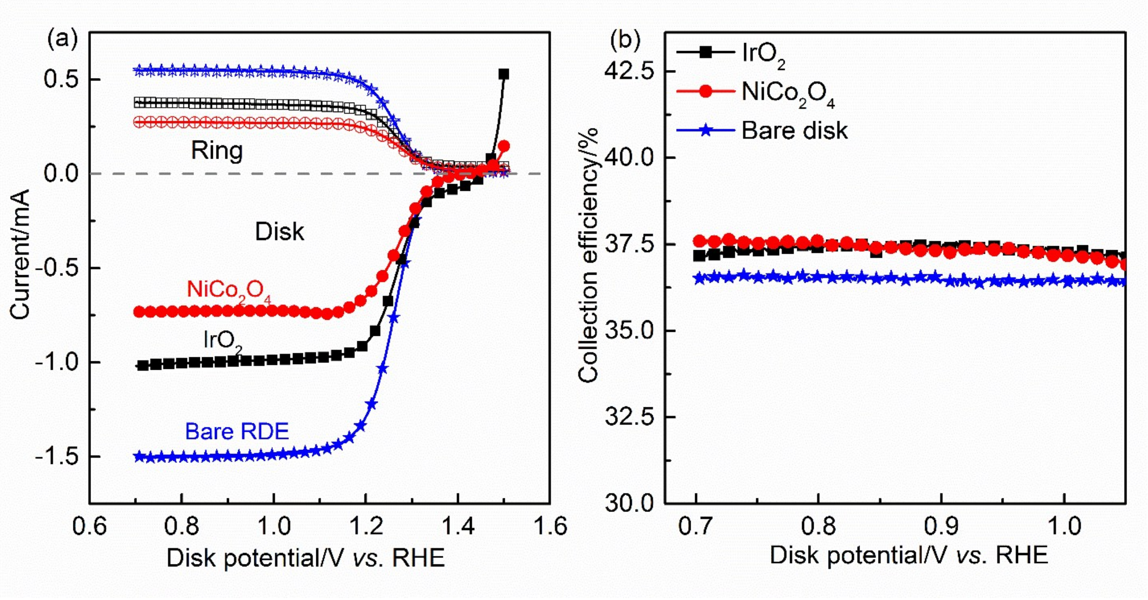

Fig. S9 RRDE evaluation for collection efficiency. (a) RRDE voltammogram for reducing $K_3Fe(CN)_6$ (10 mM) at the disk electrode in N_2-purged 1.0 M KOH. (b) Calculated collection efficiency of RRDE with/without various catalysts deposited on the disk. Scan rate = 5 mV s^{-1}; rotating rate=1600 rpm.

Collection efficiency of RRDE

Not all species formed at the disk electrode can be transported to the ring surface. Depending on the electrode and operation conditions, a fraction of the stable species undergo an electrochemical oxidization/reduction reaction at the ring.[3] It is thus necessary to determine this fraction, namely, the collection efficiency (*N*). Although *N* can be calculated directly from electrode geometry, *N* is usually obtained experimentally to account for fabrication variation. A classic redox couple used to determine *N* is $[\mathrm{Fe(CN)_6}]^{3-}$/$[\mathrm{Fe(CN)_6}]^{4-}$ according to the following reversible reaction:

$$\left[\mathrm{Fe}\left(\mathrm{CN}\right)_6\right]^{3-} + e^- \leftrightarrow \left[\mathrm{Fe}\left(\mathrm{CN}\right)_6\right]^{4-} \quad E^0 = 0.28\,\mathrm{V}$$ * MERGEFORMAT (S5)

The voltammetry experiment is conducted in N_2-saturated 1.0 M KOH solution containing 10 mM $K_3Fe(CN)_6$. The disk electrode with and without catalysts (0.24 mg cm^{-2}) were estimated at a rotating rate of 1600 rpm. The disk potential was scanned from 1.5 V to 0.7 V at a scan rate of 5 mV s^{-1} and the ring potential was held at 1.5 V, where the reduced product $[\mathrm{Fe(CN)_6}]_4^-$ can be easily oxidized back to $[\mathrm{Fe(CN)_6}]^{3-}$. The collective current-potential voltammetry is given in Fig. S10 (a). The *N* can be calculated as:

$$N = \frac{i_\mathrm{r}}{\left|i_\mathrm{d}\right|} \times 100\%$$ * MERGEFORMAT (S6)

where i_r is the disk limiting current for reducing $[\mathrm{Fe(CN)_6}]^{3-}$, and i_d is the corresponding ring current.

As shown in Fig. S10 (b), the average *N* values used in our study can be obtained at potentials between 0.8-1.0 V. The *N* values of IrO_2 and $NiCo_2O_4$ were calculated to be 37.40 % and 37.36 %, respectively, which is very close to the theoretical value of 37 %.

TF-RRDE voltammetry

Employing the TF-RRDE method for OER, the O_2 and intermediates generated at the disk can be detected on the ring electrode. This method is frequently used to deduce the reaction mechanisms and study various EDL behaviors in terms of mass and charge transfer.[4, 5] In principle, a ring potential of 0.4 V can easily reduce the O_2 diffused from disk electrode. There are generally two types of current recorded during OER. They are the Faradaic current (i_{OER}) due to OER and non-faradaic capacitive current (i_{C}) due to charging process in the reaction interface. Therefore, the disk current (i_{d}) can be expressed as:

$$i_{\mathrm{d}} = i_{\mathrm{OER}} + i_{\mathrm{C}} \quad \text{* MERGEFORMAT (S7)}$$

The ORR current from the Pt-ring electrode can be used to determine the contribution of i_{OER} to total disk current (i_{d}). When the current of O_2 evolution is small, the OER current (i_{OER}) can be fully directed at the ring and can be expressed by Eq. S8 under the assumption that the OER-ORR pair reaction occurs via 4-electron transfer process.

$$i_{\mathrm{OER}} = {i_{\mathrm{r}}^{*}}/{N} \quad \text{* MERGEFORMAT (S8)}$$

where i_{r}^{*} is the measured ring current corrected by the background noise without Faradaic reaction, and N is the collection coefficient of RRDE. With known i_{OER} , the capacitive current ratio, ε_{c} , can be obtained. This current ratio reveals the extent to which the capacitive process is favored compared to OER.

$$\varepsilon_{\mathrm{c}} = \frac{i_{\mathrm{c}}}{i_{\mathrm{d}}} = \frac{(i_{\mathrm{d}} - {i_{\mathrm{r}}^{*}}/{N})}{i_{\mathrm{d}}} \quad \text{* MERGEFORMAT (S9)}$$

O_2 transport in the disk electrode is crucial in determining the performance of OER catalysts. With the increase of applied OER potential, a higher portion of generation O_2 can escape from the disk to electrolyte solution without being detected by the ring. Therefore, the O_2 transport efficiency in the disk electrode can be calculated by:

$$\varepsilon_{O_2} = \frac{i_{\mathrm{OER}} - {i_{\mathrm{r}}^{*}}/{N}}{i_{\mathrm{OER}}} \quad \text{* MERGEFORMAT (S12)}$$

where i_{OER} can be calculated from the disk current minus the capacitive current. In our experiment, the capacitive current, i_{c}^{*}, is obtained at 1.4 V, where no OER reaction exists. With this assumption, the O_2 transport efficiency can be re-arranged as:

$$\varepsilon_{O_2} = \frac{\left(i_{\mathrm{d}} - i_{\mathrm{c}}^{*}\right) - i_{\mathrm{r}}^{*}/N}{\left(i_{\mathrm{d}} - i_{\mathrm{c}}^{*}\right)}$$

* MERGEFORMAT (S13)

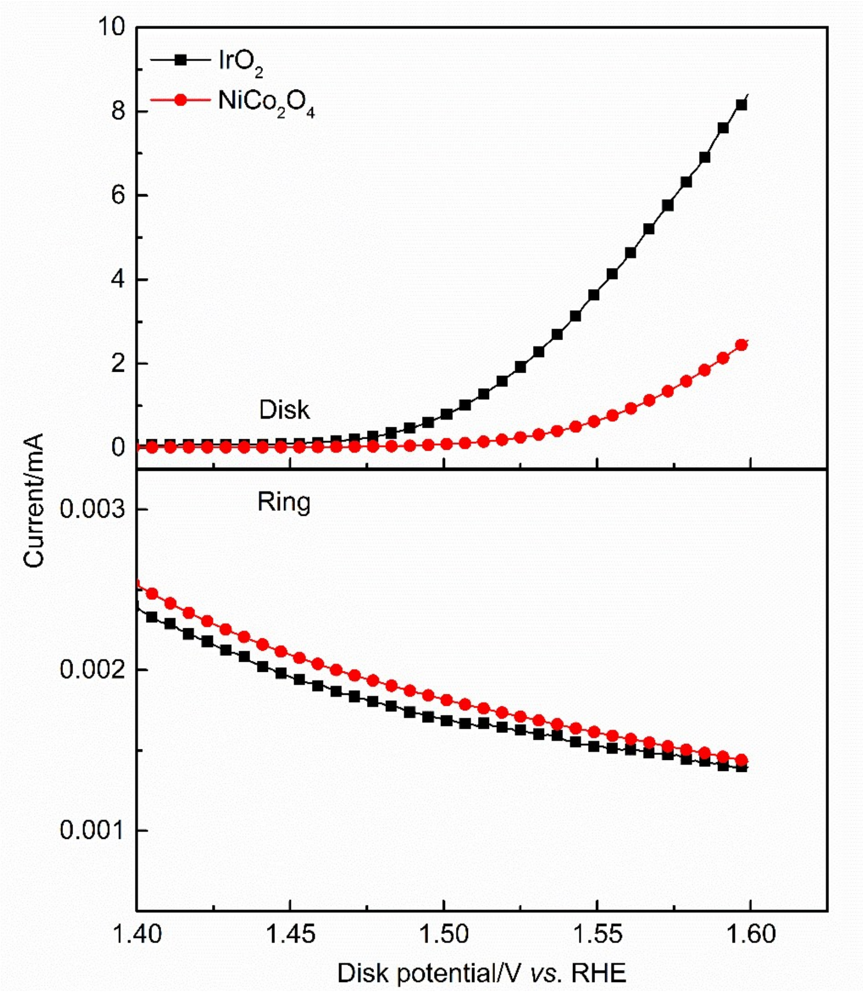

Fig. S10 RRDE voltammogram at disk electrode (at a rotating rate of 1600 rpm and a scan rate of 2 mV s^{-1}) and ring electrode (holding at 1.40 V vs. RHE).

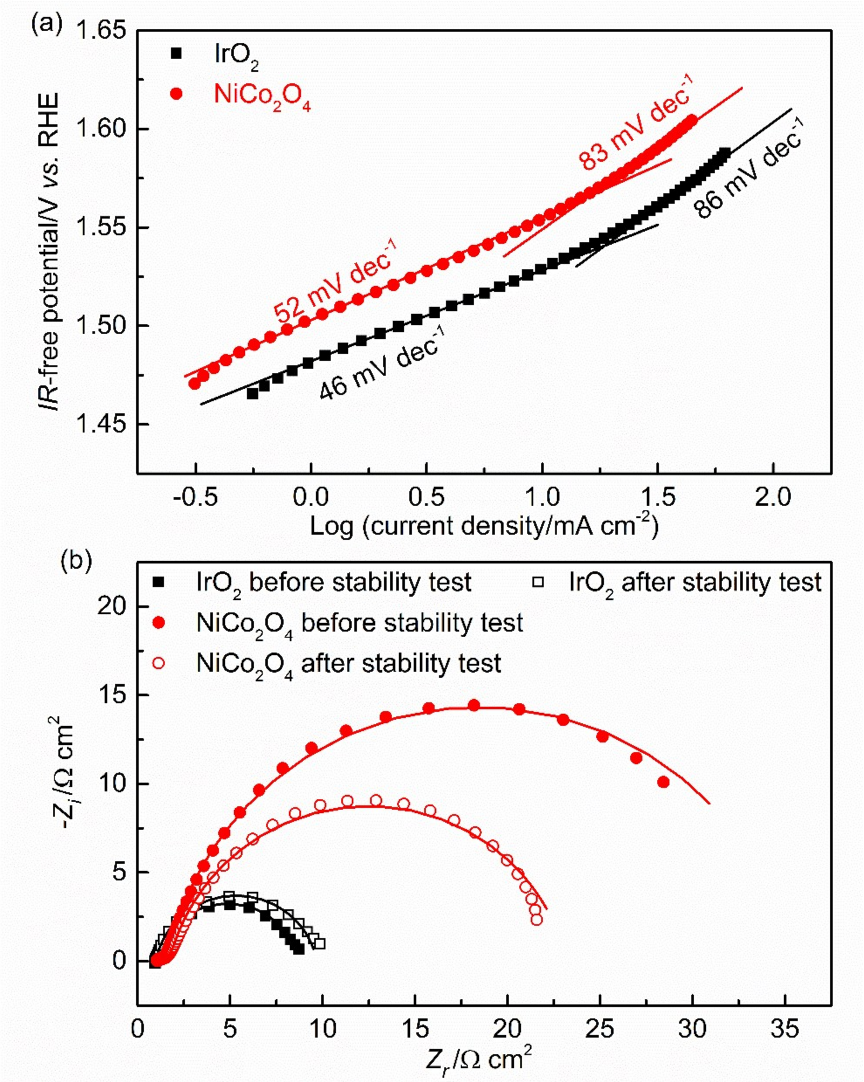

Fig. S11 Evaluation of catalyst performance after catalyst stability test. (a) *IR*-corrected Tafel plots and (b) EIS spectra at 1.5 V. Symbols - raw data; lines – linear fit to the data.

References

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