

Supporting information

Iron doping induced formation of Ni-Co-O Nanotube as Efficient Bifunctional Electrodes

Zhaohui Liu,^{*a} Xinjiang Zhang,^a Xiaona Mi,^a Zirun Yang^a and haihua Huang^{*b}

^a School of Material Science and Engineering, Yancheng Institute of Technology,

Yancheng 224051, China

^b School of Material Science and Engineering, Liaocheng University, Shandong

252059, China

*Corresponding author

Email: zhliu@ycit.edu.cn (Zhaohui Liu)

huanghaihua@lcu.edu.cn (Haihua Huang)

Electrochemical measurements details

The turnover frequency (TOF, s^{-1}) for HER was calculated with the following equation:

$$TOF=(|J| \times A)/2Fn \quad (1)$$

Where $|J|$ ($A \cdot cm^{-2}$) is the current density at a fixed voltage during the LSV measurement, A is the geometric area of the working electrode (1 cm^2), the factor of 2 is the corresponding electron transfer numbers, F is the Faraday constant ($96485 \text{ C} \cdot \text{mol}^{-1}$), and n is the number of active sites (mol).

$$n=Q/2F \quad (2)$$

The number of active sites (n) was determined by the cyclic voltammetry (CV) with a scan rate of 10 mV s^{-1} . The number of the voltammetric charges (Q) could be determined by integrating.

The turnover frequency (TOF, s^{-1}) for OER was calculated with the following equation:

$$TOF=(|J| \times A)/4Fn \quad (3)$$

$$n=Q/4F \quad (4)$$

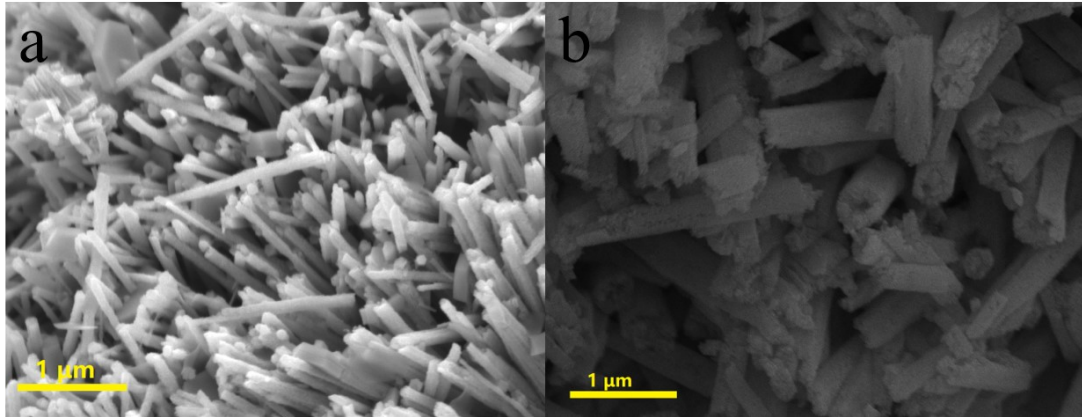


Fig. S1 (a) $\text{Fe}_3\text{-NCO}$ with an annealing temperature at 300 °C and (b) at 500 °C.

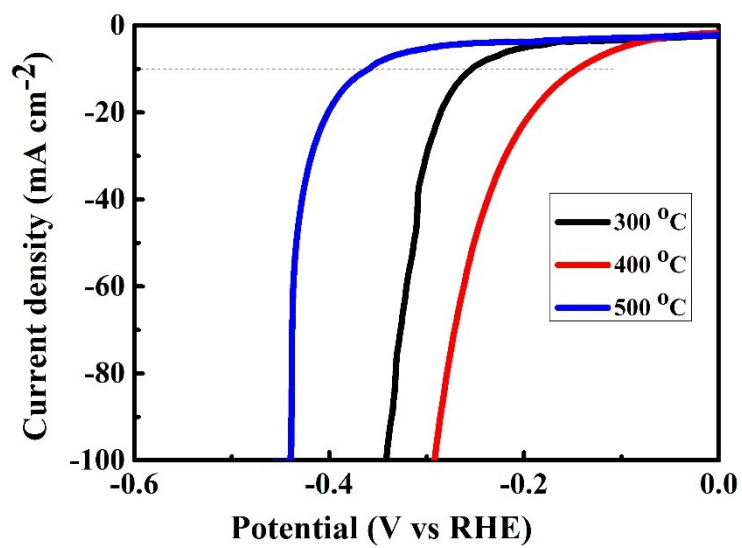


Fig. S2 LSV curves of HER at 5 mV s⁻¹ of the Fe₃-NCO at different annealing temperature.

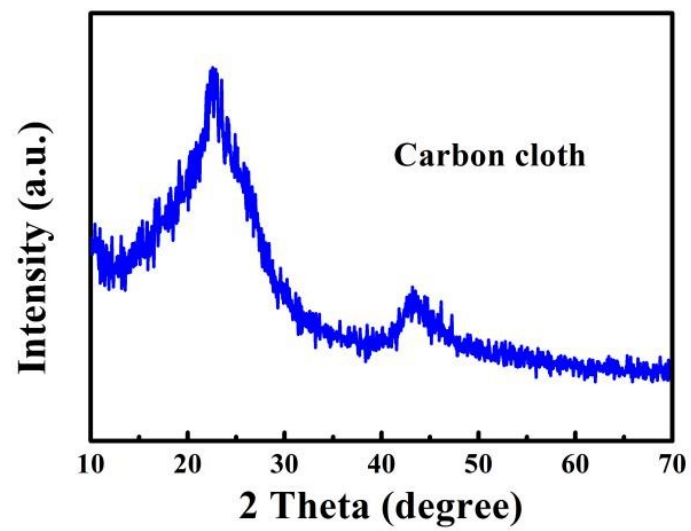


Fig. S3 XRD patterns of carbon textiles.

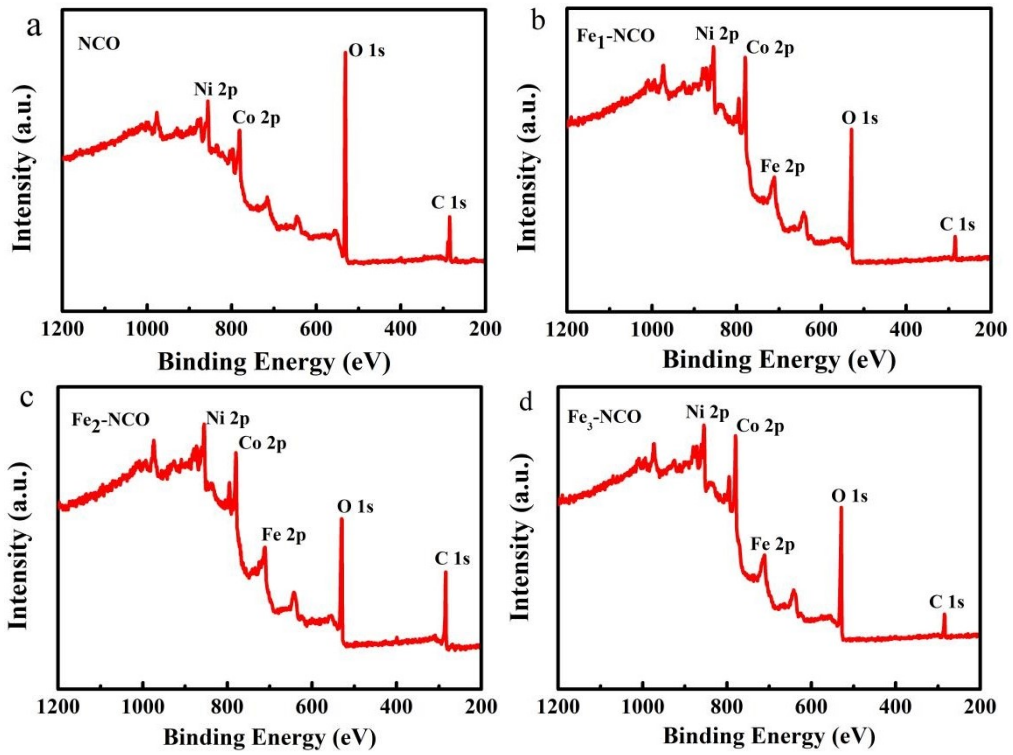


Fig. S4 Overall XPS survey spectra of as-prepared various electrocatalysts.

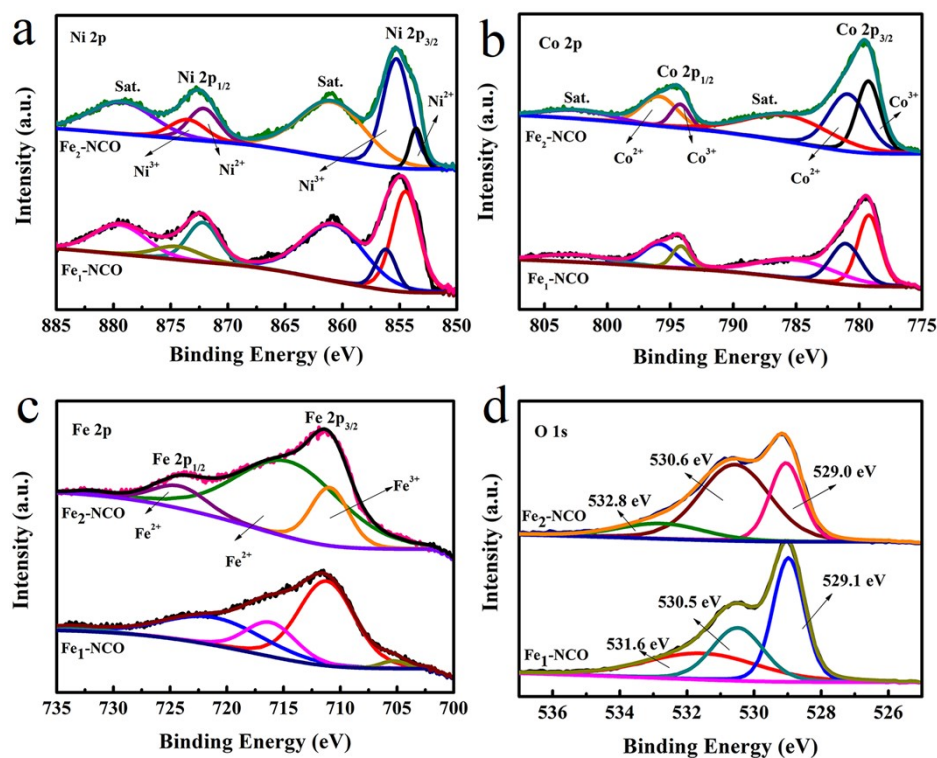


Fig. S5 (a) Ni 2p spectra of Fe₁-NCO and Fe₂-NCO, (b) Co 2p spectra of Fe₁-NCO and Fe₂-NCO, (c) Fe 2p spectra of Fe₁-NCO and Fe₂-NCO and (d) O 1s spectrum of Fe₁-NCO and Fe₂-NCO.

According to the Ni2p spectra of NiCo₂O₄, the Ni2p spectrum in Figure S4a was composed of two spinorbit doublets and two satellite, the peaks of Fe₁-NCO at about 854.9 and 872.9eV were corresponded to Ni²⁺, whereas those at 856.2 and 874.9 eV were fitted with Ni³⁺. For Fe₂-NCO the peaks at 854.7 and 873.1 eV was fitted with Ni²⁺, while those at 855.9 and 874.7 eV belongs to Ni³⁺, respectively.¹ The Co2p

spectrum in Figure S4b was fitted into both Co 2p_{1/2} and Co 2p_{3/2} with a shakeup satellite for each. The peaks of Fe₁-NCO situated at 781.9 and 796.9 eV can be indexed into Co²⁺ species, while those at 779.7 and 794.8 eV correspond to Co³⁺.² The spin-orbit located at 781.8 and 797.1 eV of Fe₂-NCO can be ascribed to Co²⁺ and the binding energies found at 779.9 and 795.8 can be attributed to Co³⁺. Compared to pristine NiCo₂O₄ (NCO), the binding energies of Ni 2p and Co 2p in Fe₁-NCO and Fe₂-NCO were shifted to lower values. As for the Fe 2p spectrum of Fe₁-NCO, the characteristic peaks of Fe³⁺ occur at 711.4 eV, while that of Fe₂-NCO at 711.6 eV, respectively.³

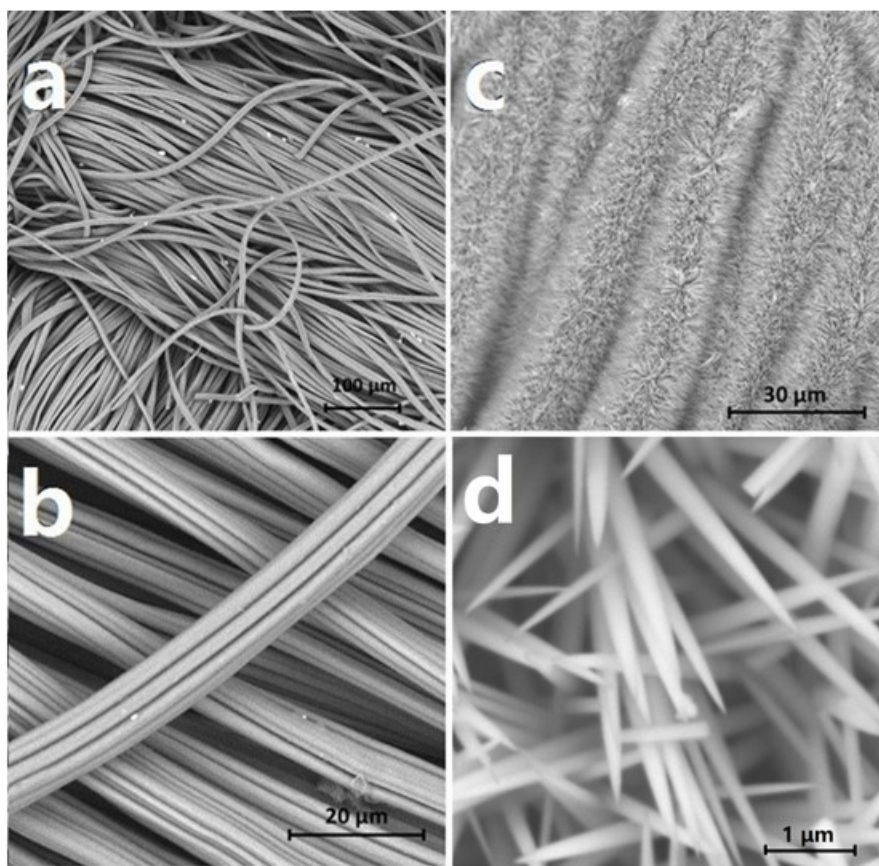


Fig. S6 Low (a) and high (b) magnification of SEM images of the carbon textiles, Low (c) and high (d) magnifications of the NCO.

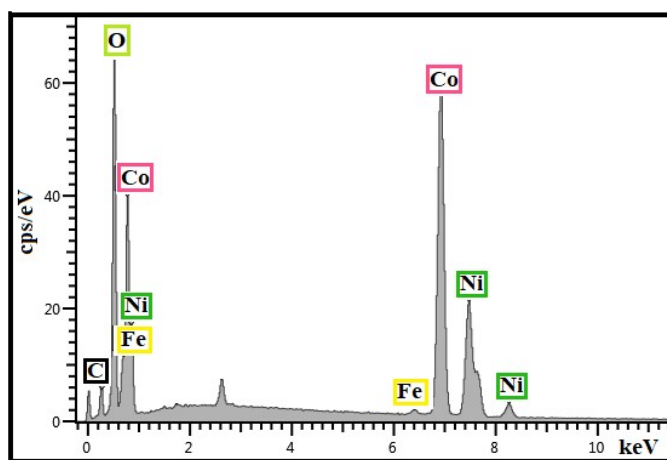


Fig. S7 EDS of Fe₃-NCO.

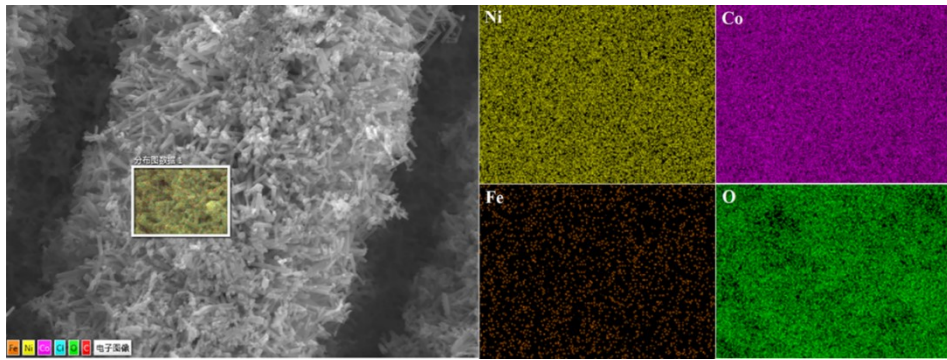


Fig. S8 The element mapping analysis of Fe₃-NCO.

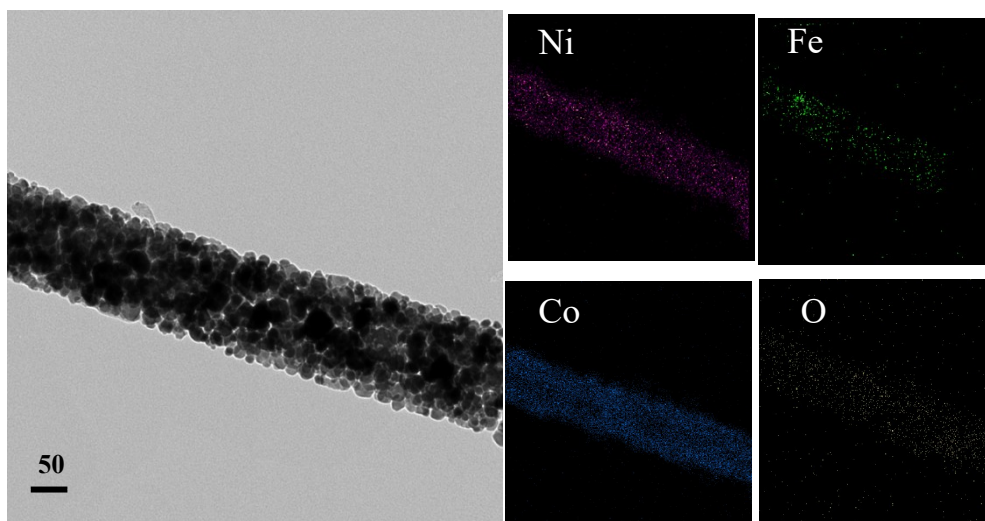


Fig. S9 The EDS mapping images of Fe₃-NCO.

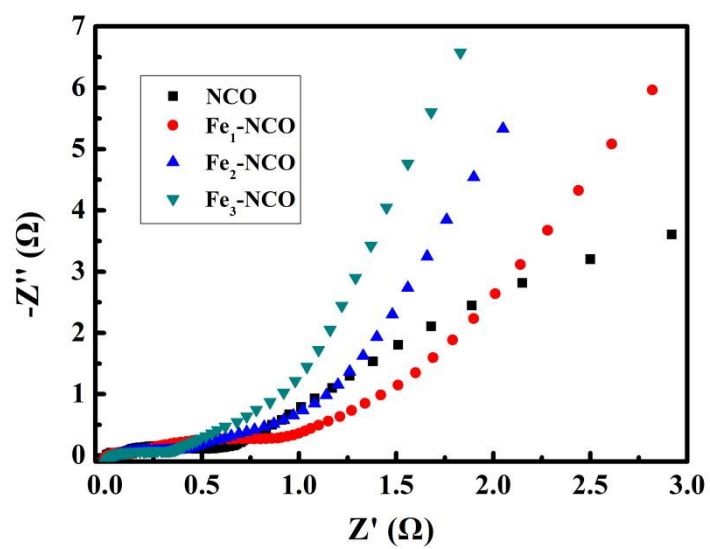


Fig. S10 Nyquist plots of various catalysts in 1 M KOH.

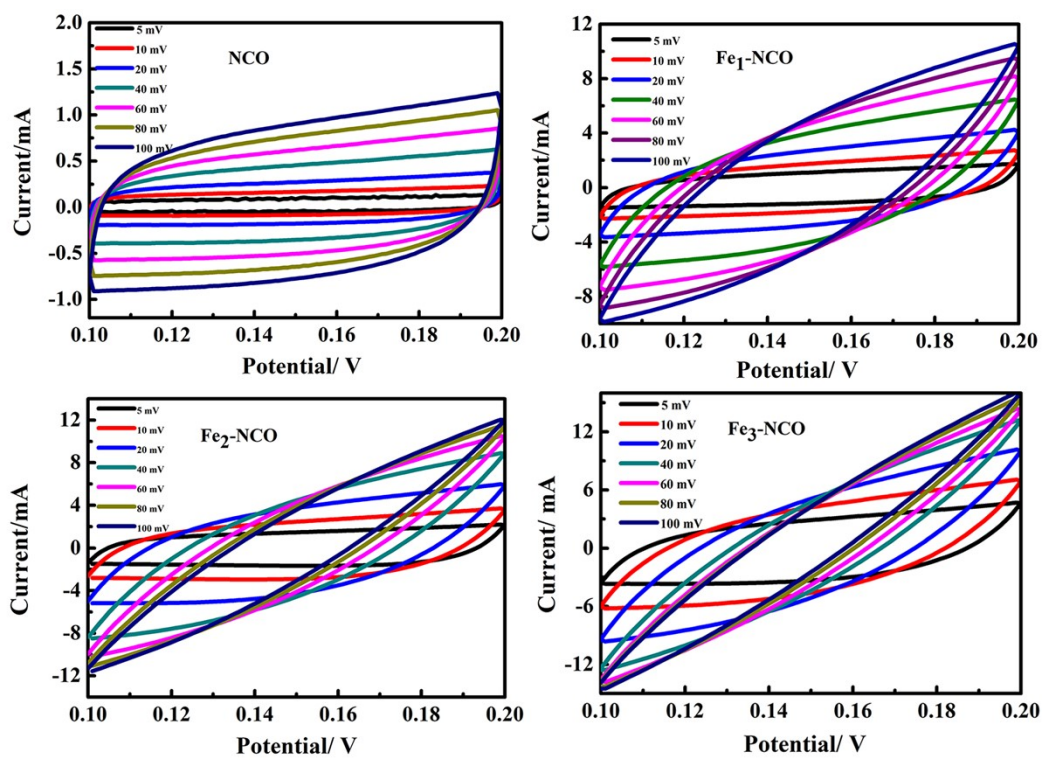


Fig. S11 CV curves of the various catalysts for the OER in 1 M KOH.

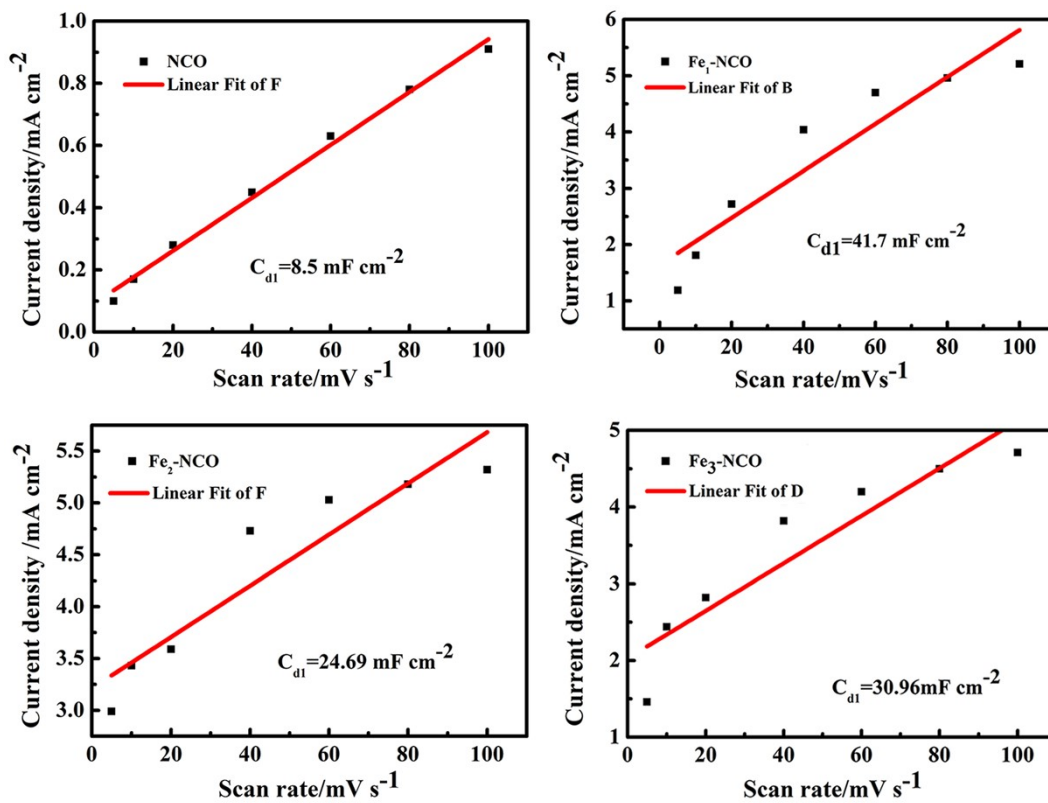


Fig. S12 ECSA of the various catalysts in 1 M KOH.

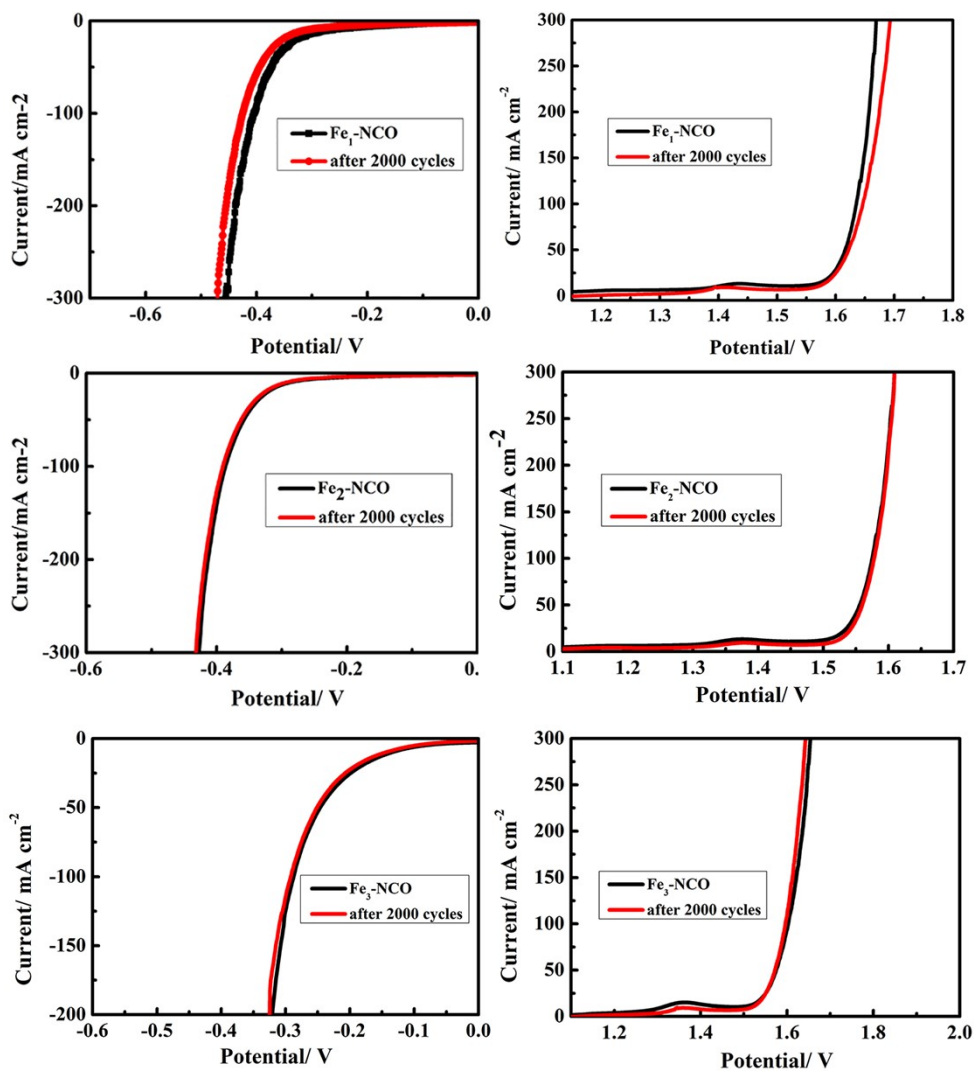


Fig. S13 LSV curves of the various electrodes for HER and OER before and after 2000

continuous cycles.

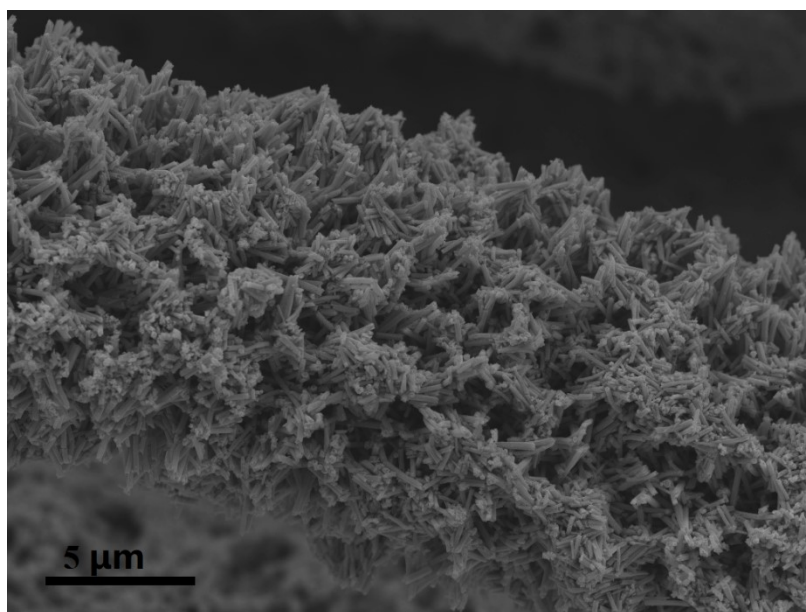


Fig. S14 SEM image of Fe₃-NCO after 2000 continuous cycles in the alkaline electrolyte.

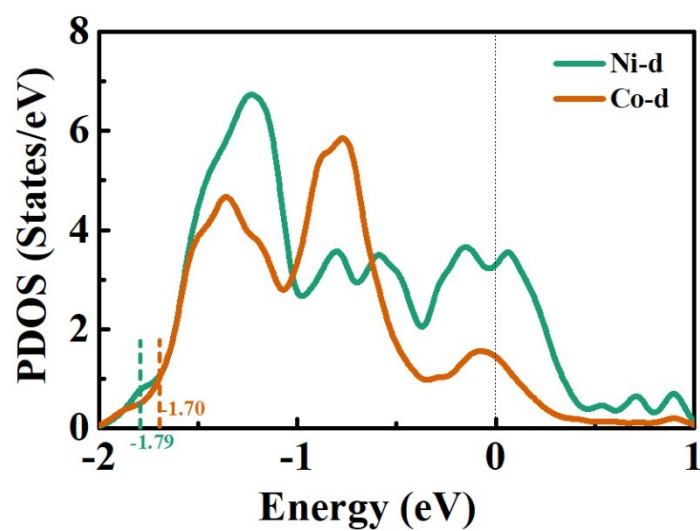


Fig.S15 The projected density-of-states of d orbitals of Ni, Co sites with aligned Fermi level in NCO.

Table S1. Elemental compositions of various samples

Sample	Ni (wt%)	Co (wt%)	Fe (wt%)	Atomic ratio of Ni, Co
NCO	22.26	46.86		1:2.11
Fe ₁ -NCO	20.20	42.90	5.63	1:2.12
Fe ₂ -NCO	10.28	22.49	7.21	1:2.18
Fe ₃ -NCO	12.99	30.15	9.36	1:2.32

References

- 1 Z. Liu, H. Tan, D. Liu, X. Liu, J. Xin, J. Xie, M. Zhao, L. Song and H. Liu, *Adv. Sci.* 2019, **6**, 1801829.
- 2 M. Yu, S. Zhou, Z. Wang, J. Zhao and J. Qiu, *Nano Energy*, 2018, **44**, 181-190.
- 3 J. Zhang, X. Shang and H. Ren, *Adv. Mater.* 2019, **31**, 1905107.