Supplementary Information (SI) for Chemical Science.

Supporting information

Dynamic and Interconnected Influence of Dissolved Iron on the Performance of Alkaline Water Electrolysis

Fubiao Di,[a]‡ Cong Chen,[a]‡ Junxia Shen,[a] Zhihe Wei,[b] Wen Dong,[a] Yang Peng,[b] Ronglei Fan,*[a] Mingrong Shen,*[a] and Pierre-Yves Olu*[c]

[a] School of Physical Science and Technology, Jiangsu Key Laboratory of Frontier Material Physics and Devices, Collaborative Innovation Center of Suzhou Nano Science and Technology, Soochow University, 1 Shizi Street, Suzhou 215006, China. E-mail: rlfan@suda.edu.cn (R. Fan), mrshen@suda.edu.cn (M. Shen)

[b] Soochow Institute of Energy and Material Innovations, College of Energy, Provincial Key Laboratory for Advanced Carbon Materials and Wearable Energy Technologies, Soochow University, 688 Moye Road, Suzhou 215006, China

[c] John Cockerill Hydrogen S. A, 1 Rue Jean Potier, 4100 Seraing, Belgium. E-mail: pierre-yves.olu@johncockerill.com (P.-Y. Olu)

‡ Both authors contributed equally to this manuscript.

Experimental section

Materials

Ethanol (C_2H_5OH), potassium hydroxide (KOH), hydrochloric acid (HCl) and Anhydrous iron sulfate $Fe_2(SO_4)_3$ were of analytical grade and used without further treatment. Deionized water with a resistivity of about 18.5 MΩ was used throughout the experimental processes. Bare nickel mesh (BN) and Raney Ni mesh (RN) were purchased from DeQing-HengChuan New Material Technology (Suzhou) Co., Ltd.

Purification of KOH

The purified KOH electrolyte was obtained by electrodeposition. Fresh 30 wt.% KOH solution were pre-electrolyzed for ≈48 h to remove the electrolyte impurities. A nickel cathode and nickel anode with a geometric surface area of ≈ 50 cm^2 was used, while the applied current was 500 mA/cm^2.

Electrochemical measurements

The 48h constant current experiment was carried out in a polytetrafluoroethylene (PTFE) electrolytic cell, and the electrodes were pressed on the PPS diaphragm, all electrodes are 1x1cm^2 in size (Fig. S20). The individual potential of electrode is measured by introducing a Hg/HgO reference electrode, measuring the potential difference between the Hg/HgO reference electrode and the target electrode by open-circuit potential working mode.

The measurements of LSV were performed in a standard three-electrode system, which consisted of a working electrode (BN or RN), counter electrode (graphite plate) and reference electrode (Hg/HgO). All the measurements were tested in 30 wt% KOH solution at 60 °C. The potentials were converted to the potentials referring to the reversible hydrogen electrode (RHE), according to following equation:

$$V_{RHE} = V_{Hg/HgO} + 0.098\ V + pH \times 0.059\ V$$

100% IR compensation corrections were applied on the LSV curves based on the obtained value of R through electrochemical impedance spectroscopy (EIS). EIS was tested at the frequence from 0.1 Hz to 100 KHz.

Cycle voltammetry (CV) measurements were used to assess corresponding electrochemically active surface area (ECSA), double layer capacitance (C_{dl}) can be obtained through CV curves, and then ECSA is calculated according to following equation: $ECSAs = \frac{C_{dl}}{C_S} \times$ A, (C_s: 0.04 mF cm^{-2} , and A: 1 cm^2).

Material characterization

Scanning electron microscopy (SEM) images and corresponding energy dispersive X-ray spectroscopy (EDX) elemental mapping were acquired on a Su-8010, Hitachi-SEM. Surface chemical compositions of samples were checked by XPS (ESCALAB 250Xi, Thermo). Raman spectroscopy was performed with HR800, Jobin Yvon (λ=532 nm). X-ray diffraction (XRD) analysis of all electrodes (D/MAX-2000PC, Japanese Rigaku) were carried out in virtue of an X-ray diffractometer (Cu Kα radiation). Concentration of ions was carried out through Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES).

Calculation of the improved power efficiency

In purified KOH, compared to BN//BN electrolyzer, the improved power efficiency ($\Delta\eta$) of RN//BN electrolyzer is as follows:

$$\Delta\eta = \frac{\Delta V}{2.44\ V} = \frac{(2.44 - 2.17)\ V}{2.44\ V} = \frac{0.27\ V}{2.44\ V} \approx 11.1\% \qquad t=48h$$

When the purified electrolyte is initially added with 150M Fe(III), the improved power efficiency ($\Delta\eta$) of BN//BN electrolyzer is as follows:

$$\Delta\eta = \frac{\Delta V}{2.44\ V} = \frac{(2.44 - 2.03)\ V}{2.44\ V} = \frac{0.41\ V}{2.44\ V} \approx 16.8\% \qquad \text{t=48h}$$

When the purified electrolyte is initially added with 150M Fe(III), the improved power efficiency ($\Delta\eta$) of RN//BN electrolyzer is as follows:

$$\Delta\eta = \frac{\Delta V}{2.17\ V} = \frac{(2.17 - 1.90)\ V}{2.17\ V} = \frac{0.27\ V}{2.17\ V} \approx 12.4\% \qquad \text{t=48h}$$

When Fe(III) is periodically added to the purified electrolyte, the improved power efficiency ($\Delta\eta$) of BN//BN electrolyzer is as follows:

$$\Delta\eta = \frac{\Delta V}{2.43\ V} = \frac{(2.43 - 1.96)\ V}{2.43\ V} = \frac{0.47\ V}{2.17\ V} \approx 19.3\% \qquad \text{t=48h}$$

Calculation of energy consumption

The volume per mole hydrogen gas was 22.4×10^{-3} Nm^3 at standard state. The electric quantity (***Q***) to produce 1 Nm^3 H_2 can be calculated using formula (1) (***V***: volume, unit: *L*; $\boldsymbol{N_A}$: Avogadro constant). When the current (***I***) is 0.4 A, the required time (***T***, unit:s) can be obtained by formula (2). And with the voltage (***V***) is determined, the energy consumption (***E***) can be calculated by formula (3). When the voltage improves Δ***U***, the energy consumption decreases Δ***E***.

For BN//BN electrolyzers, when continuously adding Fe(III) into the electrolyte, the final voltage is about 1.95V (***U*** = 1.95 V), and without Fe(III) addition, the final voltage is about 2.42 V, (Δ***U*** = 0.47 V):

$$Q = \frac{V}{22.4} \times N_A \times 2 = \frac{1000}{22.4} \times 6.02 \times 10^{23} \times 2 = 5.375 \times 10^{25} \qquad (1)$$

$$T = \frac{Q}{I \times 6.24 \times 10^{18}} = \frac{5.375 \times 10^{25}}{0.4 \times 6.24 \times 10^{18}} = 2.15 \times 10^{7}\ s \qquad (2)$$

$$E = \frac{UIT}{1000 \times 3600} = \frac{2.42 \times 0.4 \times 2.15 \times 10^{7}}{1000 \times 3600} = 5.79\ kWh \qquad (3)$$

$$\Delta E = \frac{\Delta UIT}{1000 \times 3600} = \frac{0.47 \times 0.4 \times 2.15 \times 10^{7}}{1000 \times 3600} = 1.12\ kWh \qquad (4)$$

$$\frac{\Delta E}{E} \approx 19.3\%$$

When continuously adding Fe(III) into the electrolyte, the performance of RN//BN electrolyzers (1.86 V) is improved about 0.09 V (Δ***U*** =:0.09 V) than BN//BN electrolyzers (1.95 V):

$$\Delta E = \frac{\Delta UIT}{1000 \times 3600} = \frac{0.09 \times 0.4 \times 2.15 \times 10^{7}}{1000 \times 3600} = 0.22\ kWh$$

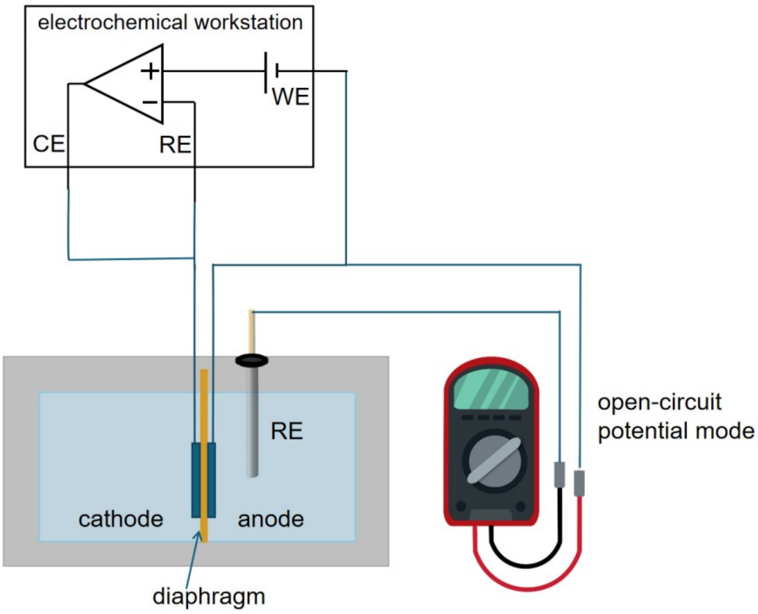

Fig. S1 The schematic picture of dynamic monitor.

During the operation of the electrolyzer, the reference electrode was inserted into the electrolyte. The potential difference between the anode (or cathode) and the reference electrode is the potential (V vs. Hg/HgO) of anode or cathode using the open-circuit potential mode.

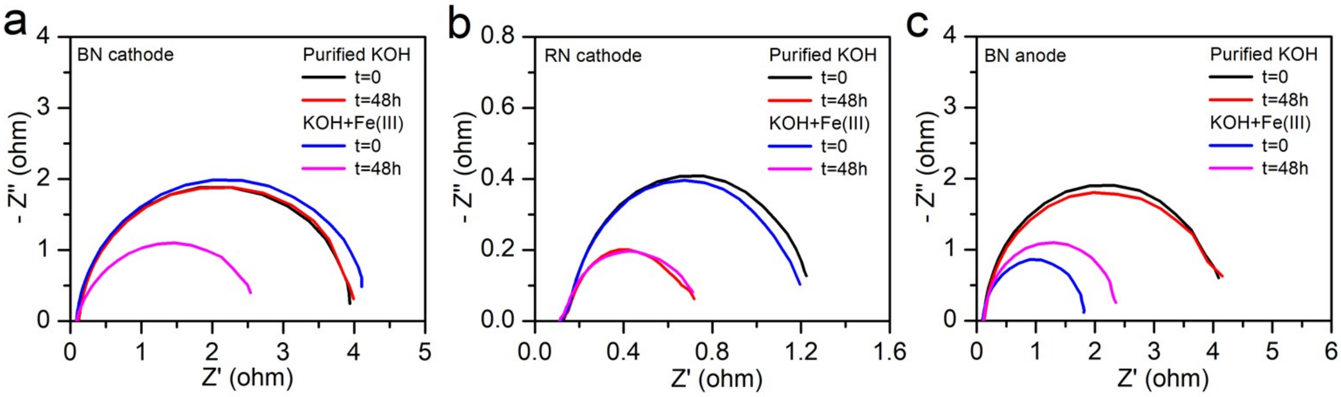

Fig. S2 Nyquist plots of (a) BN cathode, (b) RN cathode and (c) BN anode before (t=0 h) and after (t=48 h) constant current test in purified 30 wt.% KOH with and without 150 μM Fe(III) salt.

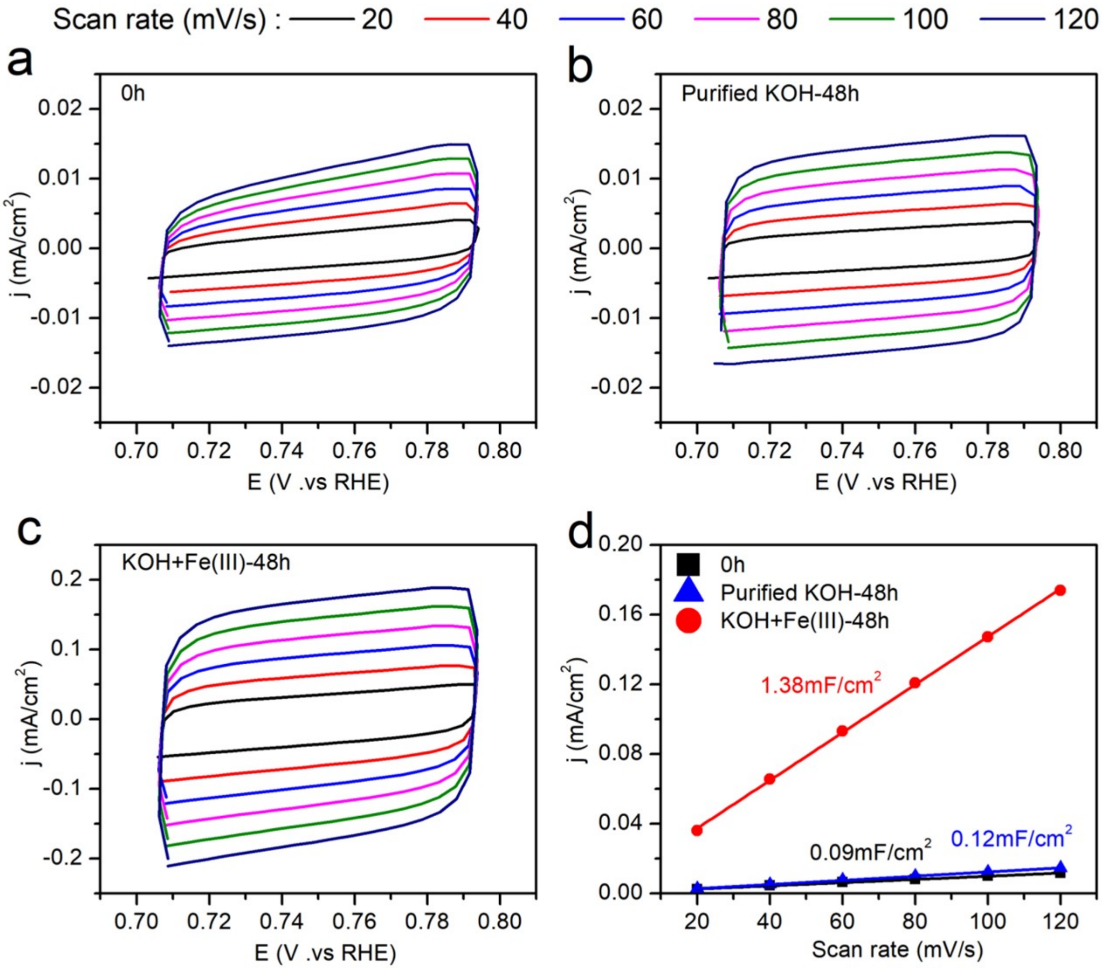

Fig. S3 The cyclic voltammetry of BN cathode at the scan rates of 20, 40, 60, 80, 100 and 120 mV/s in the window without Faradaic current for (a) 0h, (b) purified KOH-48h, (c) KOH+Fe(III)-48h, (d)Double-layer capacitances.

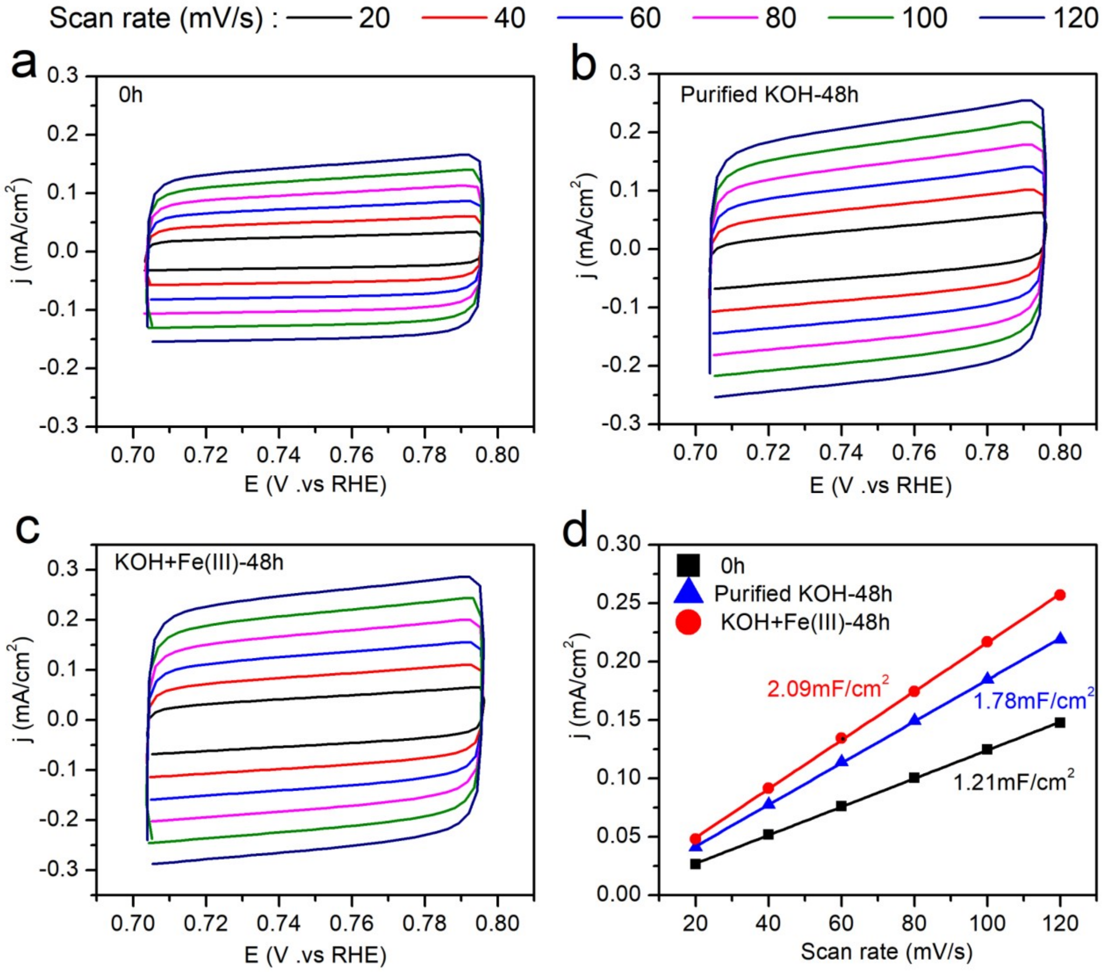

Fig. S4 The cyclic voltammetry of RN cathode at the scan rates of 20, 40, 60, 80, 100 and 120 mV/s in the window without Faradaic current for (a) 0h, (b) purified KOH-48h, (c) KOH+Fe(III)-48h, (d) Double-layer capacitances.

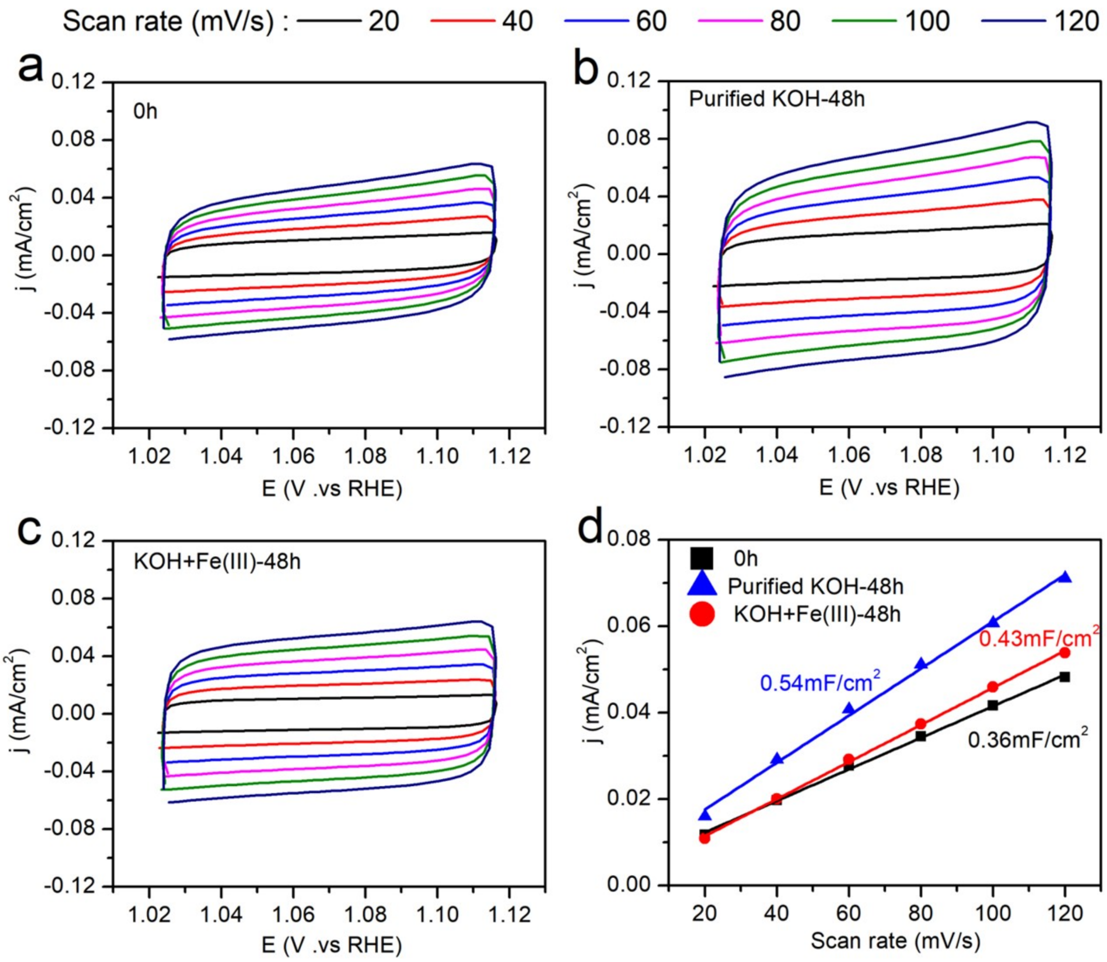

Fig. S5 The cyclic voltammetry of BN anode at the scan rates of 20, 40, 60, 80, 100 and 120 mV/s in the window without Faradaic current for (a) 0h, (b) purified KOH-48h, (c) KOH+Fe(III)-48h, (d) Double-layer capacitances.

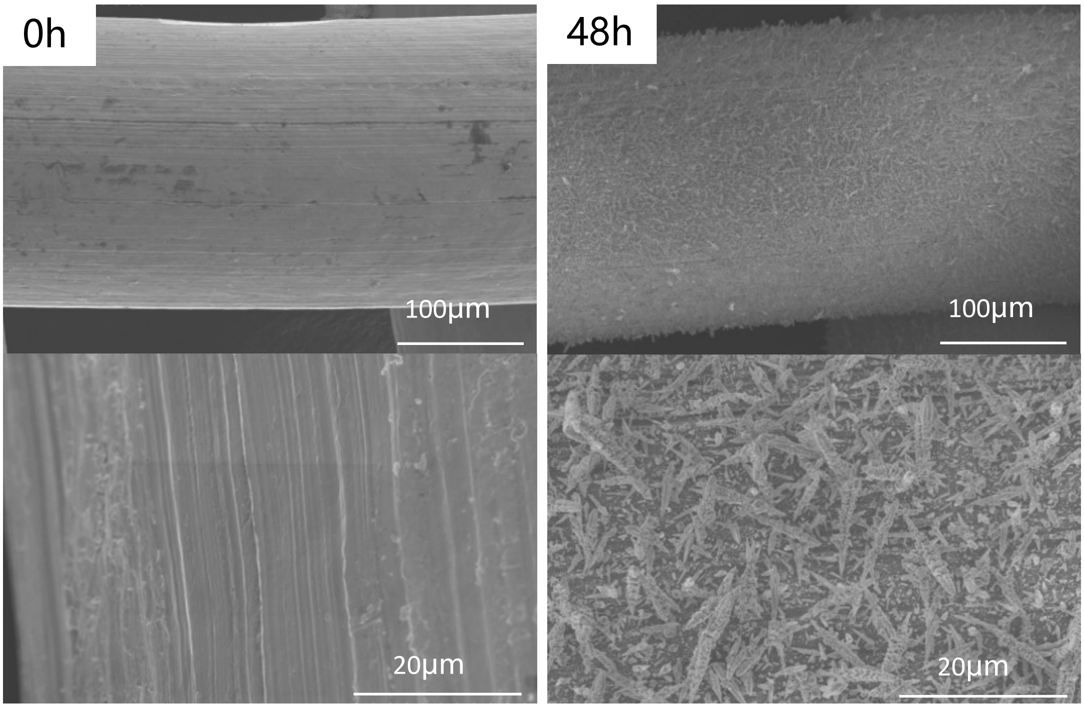

Fig. S6 SEM images with different magnifications of BN cathode tested under 0h and KOH+Fe(III)-48h

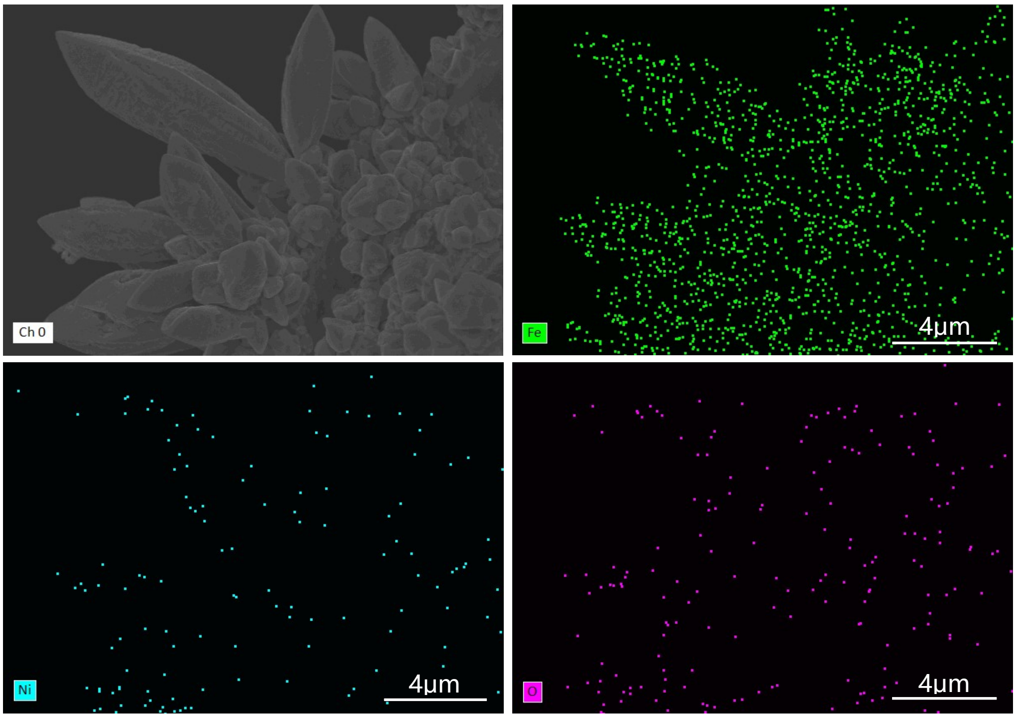

Fig. S7 EDX of BN cathode tested under KOH+Fe(III)-48h.

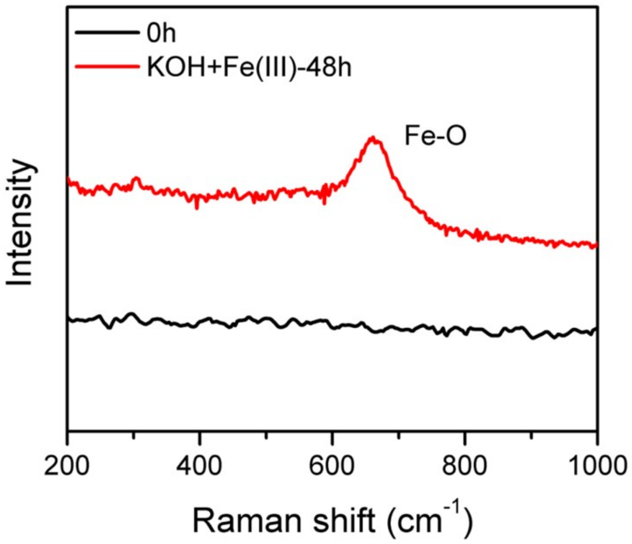

Fig. S8 Raman spectra of BN cathode tested under 0h and KOH+Fe(III)-48h.

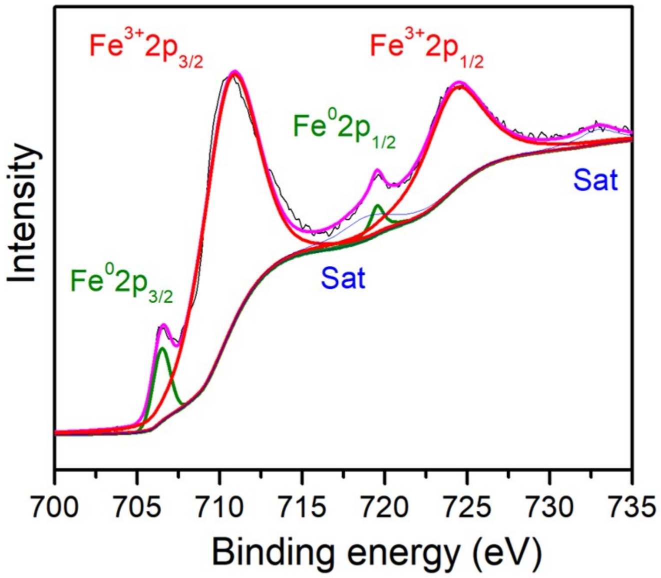

Fig. S9 XPS of BN cathode tested under KOH+Fe(III)-48h.

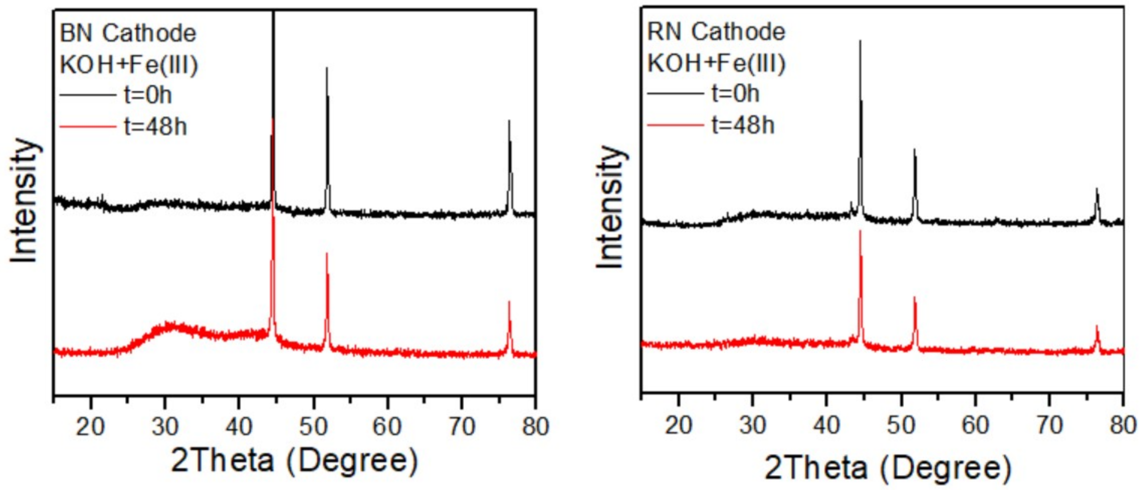

Fig. S10 XRD patterns of (a) BN cathode (b) RN cathode.

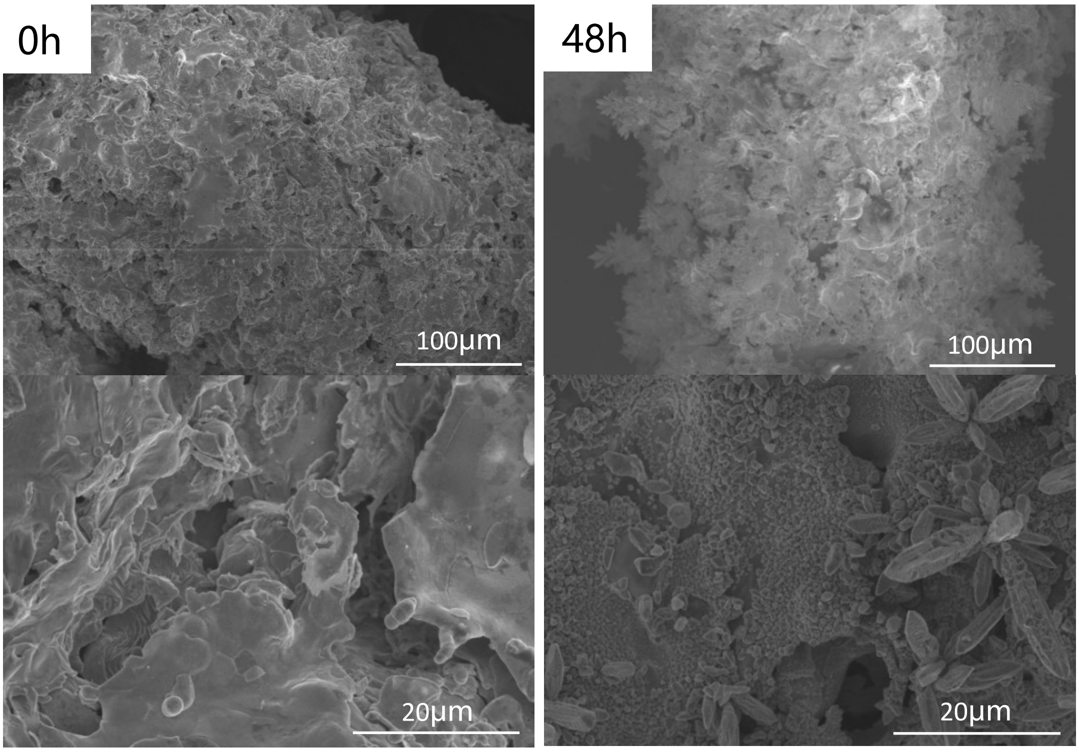

Fig. S11 SEM images with different magnifications of RN cathode tested under 0h and KOH+Fe(III)-48h.

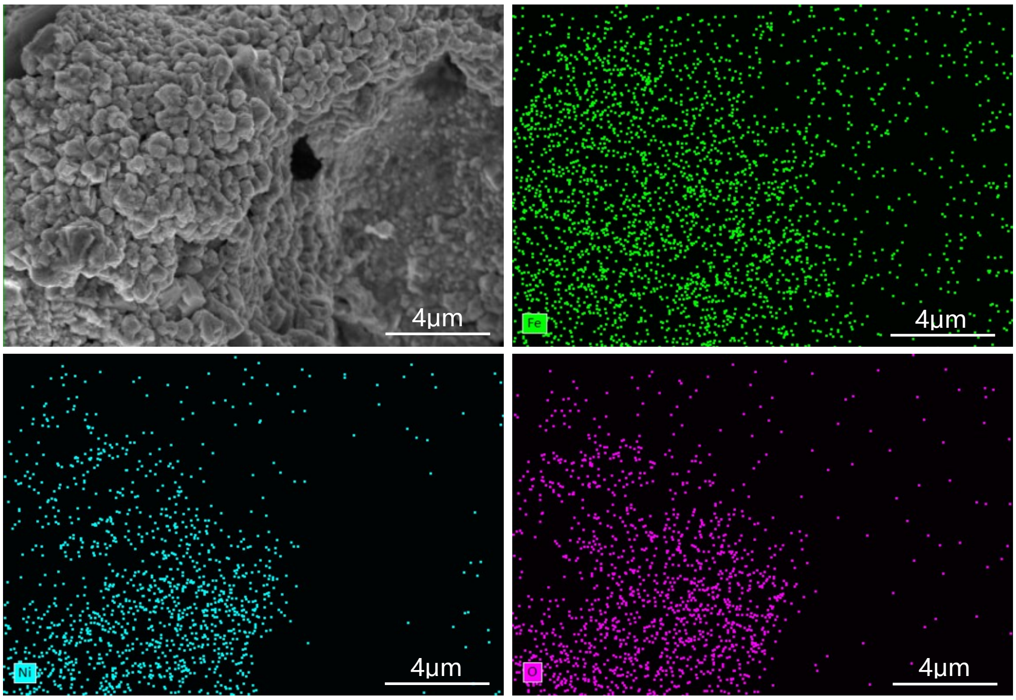

Fig. S12 EDX of RN cathode tested under KOH+Fe(III)-48h.

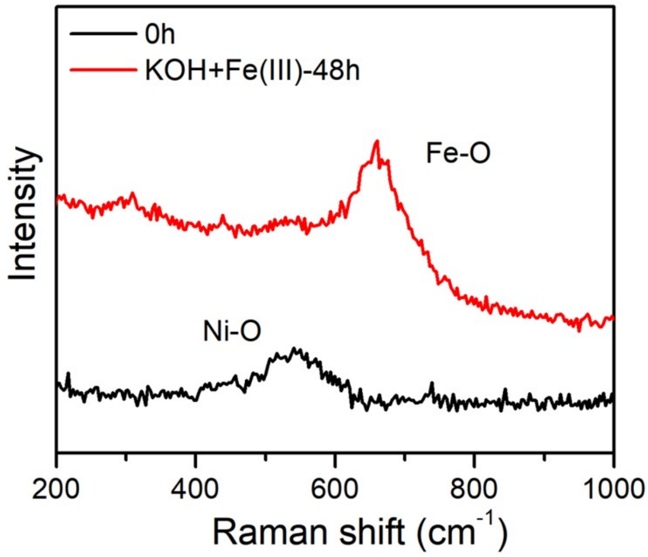

Fig. S13 Raman spectra of RN cathode tested under 0h and KOH+Fe(III)-48h.

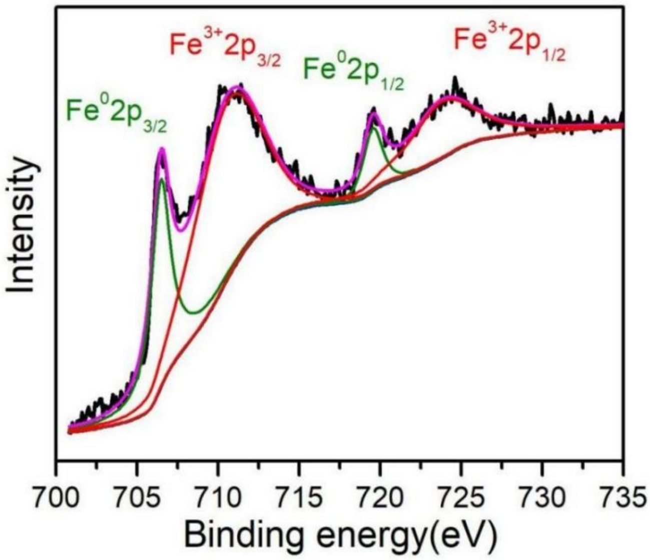

Fig. S14 XPS of RN cathode tested under KOH+Fe(III)-48h.

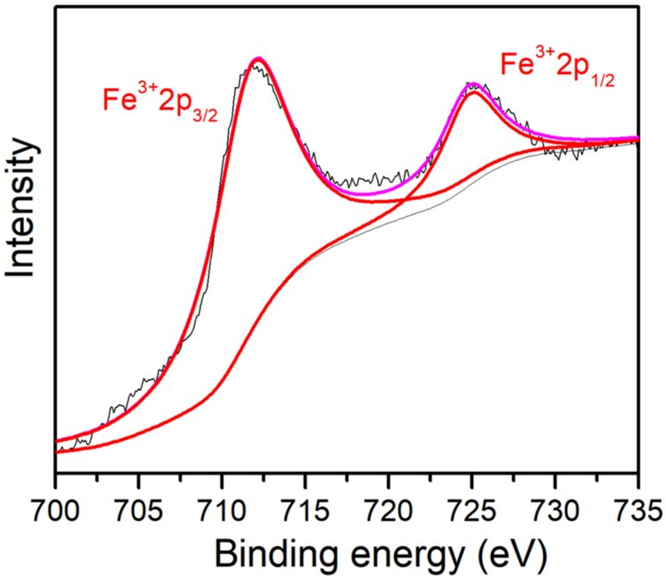

Fig. S15 XPS of BN anode tested under KOH+Fe(III)-48h.

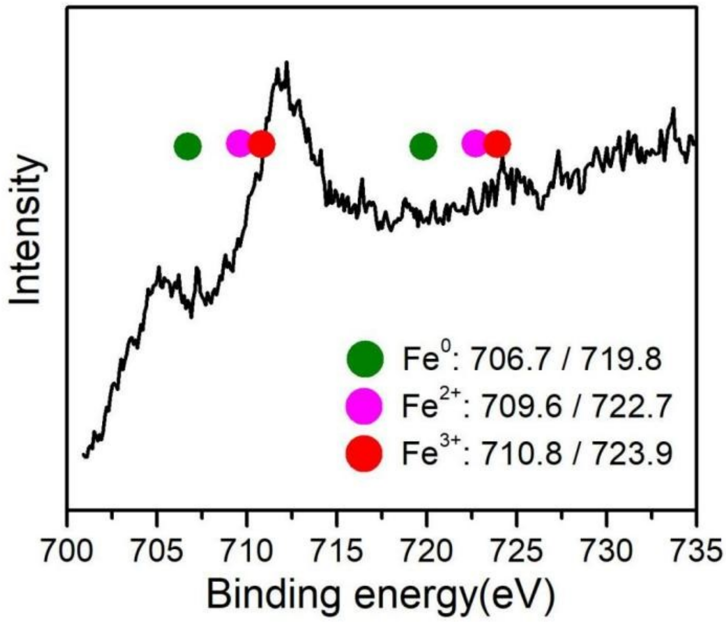

Fig. S16 XPS of BN anode tested for 0h, there is no typical Fe peak, which is basically the auger peak of Ni.

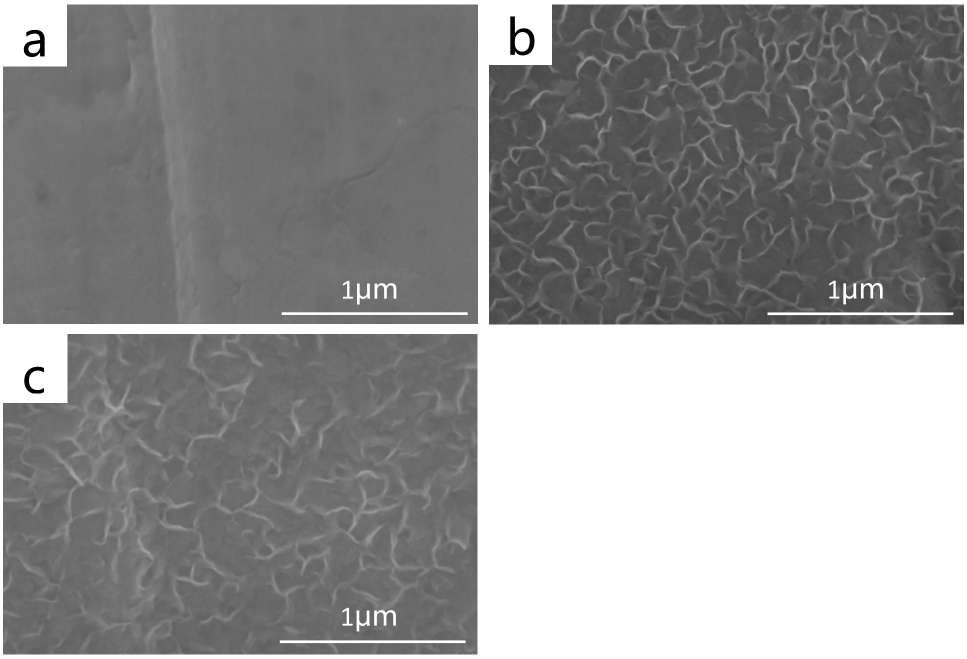

Fig. S17 SEM images of BN anode tested under (a) 0h, (b) purified KOH-48h, (c) KOH+Fe(III)-48h.

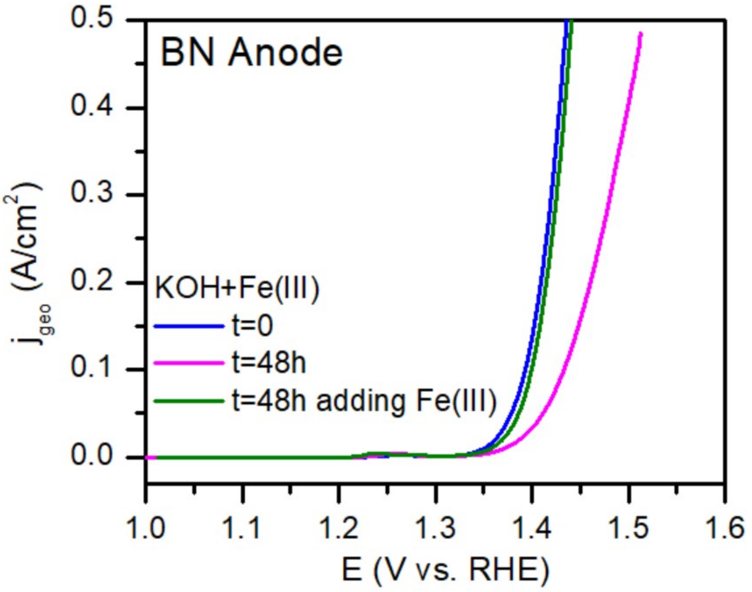

Fig. S18 The LSV curves of BN anode under different test conditions. (Blue line: purified 30 wt.% KOH with 150 μM Fe(III) salt for 0h; magenta line: purified 30 wt.% KOH with 150 μM Fe(III) salt for 48h; green line: added the same amount of Fe ions into electrolyte after 48 h.

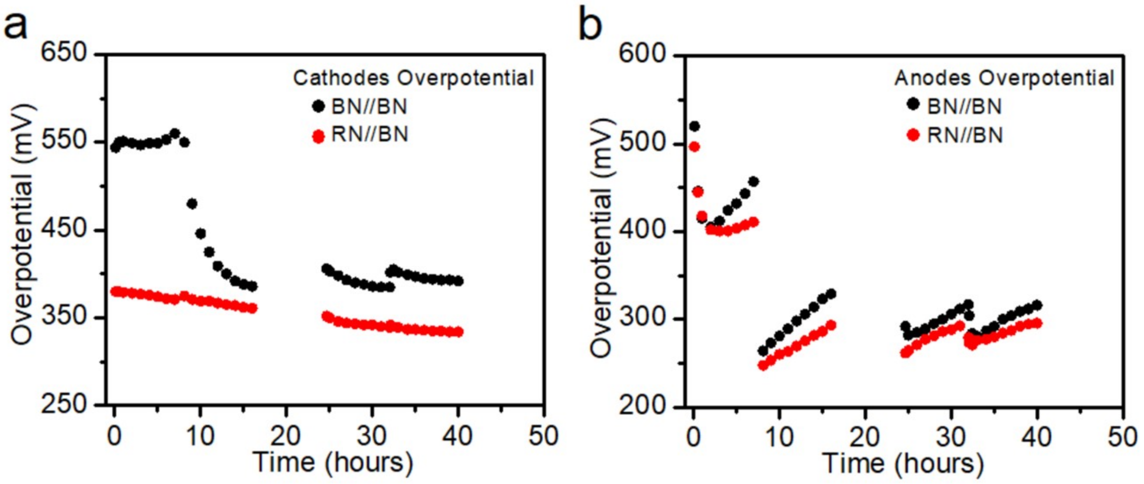

Fig. S19 (a) cathode overpotentials (taken against 0 V vs. RHE) and (b) anode overpotentials (taken against 1.23 V vs. RHE) of BN//BN and RN//BN electrolyzers. (Periodical addition of 10 μM Fe(III) salt into the electrolyte)

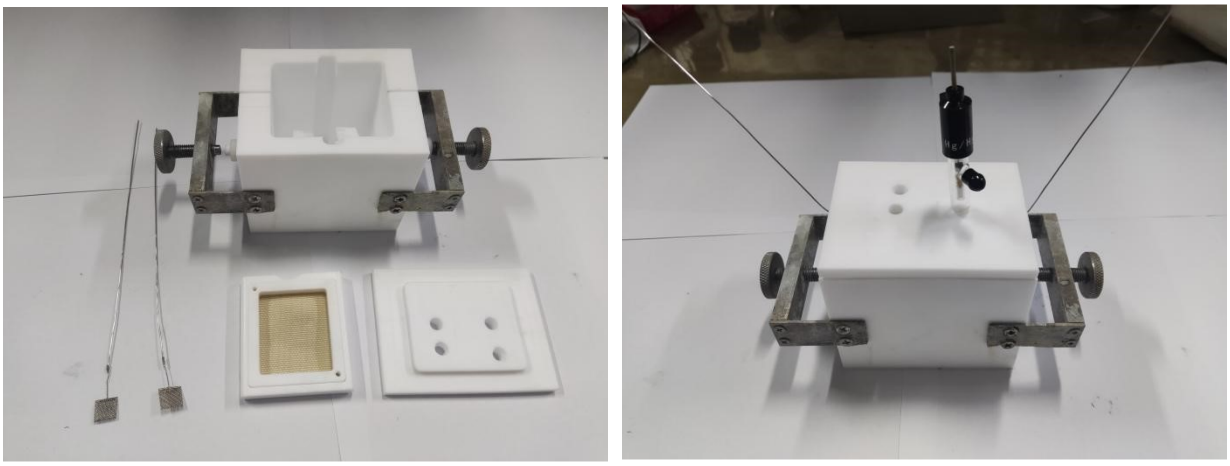

Fig. S20 The digital pictures of zero-gap cell assembly.

Table. S1 The measured solution resistance recorded from Nyquist plots.

	BN cathode	RN cathode	BN anode
Purified KOH-0h	0.123	0.130	0.105
Purified KOH-48h	0.114	0.121	0.123
KOH+Fe(III)-0h	0.090	0.127	0.106
KOH+Fe(III)-48h	0.085	0.115	0.111