Supporting Information

Sustainable Co-Production of Two Disinfectants via Hydroxide-Balanced Modular Electrochemical Synthesis Using a Redox Reservoir

Rui Wang¹, Hongyuan Sheng¹, Fengmei Wang¹,², Wenjie Li¹, David S. Roberts¹, Song Jin¹*

¹ Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, Wisconsin 53706, USA.
² CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, National Center for Nanoscience and Technology, Beijing 100190, P. R. China.

*E-mail: jin@chem.wisc.edu;

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1. Materials and Methods

Chemicals and materials

All chemicals were used as purchased without further purification. Nickel (II) nitrate hexahydrate (Ni(NO$_3$)$_2$ • 6H$_2$O, 97%), iron (III) nitrate nonahydrate (Fe(NO$_3$)$_3$ • 9H$_2$O, 98%), hexamethylenetetramine (HMT, C$_6$H$_{12}$N$_4$, 99%), Nafion 117 solution (5 %), and multi-walled carbon nanotube (MWCNT, 724769, > 95% carbon) were purchased from Sigma Aldrich. Carbon black (Super P Conductive, 99.0+%) was purchased from Alfa Aesar. TUBALL BATT NMP 0.4% (a mixture of single-wall carbon nanotubes, 0.4 wt %; polyvinylidene fluoride, 2 wt %; N-methyl-2-pyrrolidone, > 96.7 wt %) was purchased from OCSiAl. Titanium mesh was purchased from HeBei ChaoChuang Metal Mesh Co., Ltd (https://chaochuangwiremesh.en.alibaba.com/). Deionized nanopure water (18.2 MΩ·cm) from Thermo Scientific Barnstead water purification systems was used for all experiments.

Safety statement

No unexpected or unusually high safety hazards were encountered.

Synthesis of Ni(OH)$_2$

Nickel hydroxide was first synthesized by a hydrothermal method following a literature report.$^1$ Typically, 10 mmol Ni(NO$_3$)$_2$•6H$_2$O and 20 mmol HMT were dissolved in 60 mL of nanopure water and heated at 100 °C for 10 h in a sealed 80-mL Teflon-lined stainless steel autoclave. The precipitate was centrifuged and rinsed with nanopure water several times and dried in a vacuum oven at 60 °C overnight.

Synthesis of Fe-CNT

The synthesis of Fe-CNT catalyst followed a reported impregnation and reduction method with minor modifications.$^2$ In a typical synthesis, a 7.5 mM iron nitrate stock solution was first prepared by dissolving 30.3 mg Fe(NO$_3$)$_3$•9H$_2$O into 10 mL nanopure water. The carbon nanotube suspension was prepared by mixing 50 mg MWCNT with 20 mL of ethanol via sonication for 1 h until a well dispersed suspension was achieved. Then 200 μL of 7.5 mM Fe$^{3+}$ solution, making a raw atomic ratio of Fe: C around 0.1 at.%, was added dropwise into the CNT suspension under sonication for 30 min. Then the solvent was removed using a rotary evaporator, and the as-prepared
material was dried in a vacuum oven at 60 °C for 20 min to further evaporate the residual solvent. The dried Fe(NO₃)₃/CNT powder was heated up in a tube furnace to 600 °C within 20 min under a gas flow of 100 sccm Ar (UHP, Airgas) and a pressure of 1 Torr, and kept at the same temperature for another 40 min before cooling down to room temperature.

Materials characterization

Powder X-ray diffraction (PXRD) patterns of the Ni(OH)₂ samples were collected using a Bruker D8 Advance X-ray diffractometer equipped with Cu-Kα radiation. The size and morphology of the Ni(OH)₂ samples and the Fe-CNT catalysts were characterized using a scanning electron microscope (SEM, Zeiss SUPRA 55VP) equipped with an energy-dispersive X-ray spectroscopy (EDS) detector and a transition electron microscope (TEM, FEI T12) equipped with a Gatan CCD image system. X-ray photoelectron spectroscopy (XPS) of the Fe-CNT catalyst was conducted on a Thermo Fisher Scientific K-Alpha spectrometer with a monochromatic Al-Kα X-ray source.

Fabrication and electrochemical tests of the RR electrodes

The electrodes were prepared via a conventional slurry-casting method using TUBALL BATT NMP 0.4% (0.4 wt % SWCNT, 2 wt % polyvinylidene fluoride, > 96.7 wt % N-Methyl-2-pyrrolidone), super P conductive carbon, and active materials without additional polymeric binders. Typically, 70 wt % Ni(OH)₂ powder, 18 wt % Super P carbon black, 2 wt % SWCNT, and 10 wt % polyvinylidene fluoride (SWCNT and PVDF both from TUBALL BATT NMP 0.4%) were mixed and grounded into a well dispersed slurry using a mortar and pestle. The slurry was stirred at 700 rpm overnight at room temperature and then cast onto a titanium mesh current collector (150 mesh, with the thickness of ~ 230 μm). The prepared electrodes were dried in a vacuum oven at 60 °C for 12 h to remove the residual solvent. The areal mass loading of Ni(OH)₂ ranged from 1 to 23 mg cm⁻².

The electrochemical performance of the Ni(OH)₂ RR electrode was characterized in a three-electrode cell, with a Pt wire counter electrode and a Hg/HgO reference electrode, in 1 M NaOH solution. The Ni(OH)₂ electrodes were activated via 20-cycle galvanostatic charge-discharge (GCD) tests at 1C rate before all electrochemical tests, where 1C is defined as 289 mA g⁻¹ based on the theoretical capacity of Ni(OH)₂, 289 mAh g⁻¹. Cyclic voltammetry (CV) and GCD
tests of the Ni(OH)₂ electrodes were recorded on a Bio-Logic VMP-3 multichannel potentiostat. The galvanostatic cycling was performed at 289 mA g⁻¹, 578 mA g⁻¹, and 2.89 A g⁻¹ for stability characterization and the rates of 289 mA g⁻¹ to 14.5 A g⁻¹ for the kinetics characterization. For the 10-cycle galvanostatic charge-discharge tests with charging in alkaline solution and discharging in neutral solution, the Ni(OH)₂ electrode was charged to 0.6 V vs. Hg/HgO in 1 M NaOH solution at 2.89 A g⁻¹, and discharged to -0.14 V vs. SCE (0 V vs. Hg/HgO) in 1 M NaCl solution at 2.89 A g⁻¹.

**Measurements on the ion-balance ability of the RR electrodes**

The hydroxide ion-balance ability of the Ni(OH)₂ RR was evaluated in two three-electrode electrochemical configurations: a H-cell with a sintered glass filter discs (89057-758, ACE glass Incorporated, USA) and a beaker-type cell. In both configurations, a commercial dimensionally stable anode (DSA) made of iridium-ruthenium oxides covered Ti mesh (IrRuOₓ/Ti, 1×3 cm²), was used as the working electrode, a saturated calomel electrode (SCE) was used as the reference electrode, and the Ni(OH)₂ RR were used as the counter electrode. Before all tests, the Ni(OH)₂ RR was oxidized to NiOOH in 1 M NaOH solution (Table S2). For both configurations, the pH changes during electrolysis and the RR reduction in 1 M Na₂SO₄ solution and 1 M NaCl solution were monitored. As shown in Figure 3a, the OER or HCR was paired with the RR reduction in the beaker-type cell. The pH shift was recorded during the undivided electrolysis. In the H-cell, the glass filter separated the RR reduction and OER or HCR into different chambers, and the pH shift in both chambers was recorded during the electrolysis.

**Electrochemical characterization of the electrocatalytic electrodes**

All electrocatalytic characterizations were performed using a Bio-Logic SP-200 potentiostat or a Bio-Logic VMP-3 multichannel potentiostat at room temperature. Hydrogen peroxide (H₂O₂) and sodium hypochlorite (NaClO) production reactions were first evaluated in the H-cells with a sintered glass filter discs (89057-758, ACE glass Incorporated, USA) in 1M NaOH solution or 1 M NaCl solution, respectively.

**NaClO production and detection.**

The sodium hypochlorite production reaction (HCR) was evaluated in an undivided beaker-type cell in 1 M NaCl solution in a three-electrode configuration using the DSA electrode as the
working electrode, a Pt mesh as the counter electrode and a SCE as the reference electrode (Figure S10). The pH of 1 M NaCl solution was modified by 1 M HCl solution and 1 M NaOH solution to pH = 6.0, pH = 8.5, pH = 11.0, and pH = 13.3. CV curves were performed at a scan rate of 10 mV/s (Figure S11), and CA was carried out at different potentials (1.10, 1.15, 1.20, 1.25 vs. SCE) with stirring (700 r.p.m.) (Figure S11). All potentials measured against SCE were converted to the standard hydrogen electrode (SHE) using $E_{\text{SHE}} = E_{\text{SCE}} + 0.241 \text{ V}$.

The concentration of the produced NaClO was detected by iodometric titration. Specifically, the following steps were taken: 1) 1.000 g KI (>99%, Sigma-Aldrich) was first dissolved in 10 mL acetate buffer with a pH of ~ 3.7. 10 mL sample solution containing ClO⁻ was added into the above solution, and the color of the solution changed to yellow. 2) The sample solution was then titrated using 5.00 mM standard Na₂S₂O₃ solution until the yellow solution became colorless. 3) Add 1.0 mL 0.5 wt% starch solution as the indicator (the color of the sample solution became brownish red), then continuously titrate with 5.00 mM standard Na₂S₂O₃ solution until the color disappeared. Finally, the produced NaClO in the solution was calculated by the consumed volume of the 5.00 mM Na₂S₂O₃ solution via the following equation S1 and S2:

$$\text{ClO}^- + 2\text{I}^- + 2\text{H}^+ \rightarrow \text{Cl}^- + 2\text{I}^- + \text{H}_2\text{O} \quad (\text{S1})$$

$$\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-} \quad (\text{S2})$$

The FE of NaClO production reaction was then calculated based on the concentration of detected NaClO and the input charge, using the following equation:

$$\text{FE (\%)} = \frac{Q \text{ for } [\text{ClO}^-] \text{ production}}{Q_{\text{input}}} \times 100 = \frac{[\text{ClO}^-] \times \text{V} \times 2 \times 96485}{Q_{\text{input}}} \times 100 \quad (\text{S3})$$

where V, [ClO⁻], and $Q_{\text{input}}$ are the volume of the solution, the concentration of produced NaClO, and the input charge during the electrolysis, respectively.

H₂O₂ production and detection.

To prepare the Fe-CNT working electrodes, typically, 10 mg of as-prepared Fe-CNT catalyst was mixed with 1 mL of ethanol and 100 μL of Nafion 117 solution (5 %), and then sonicated for 2 h to get a well dispersed catalyst ink. A fixed volume of catalyst ink was drop-cast onto the Toray carbon paper (TGP-H-060, Fuel Cell Store) and then dried under ambient condition.
The mass loading of each electrode was around 0.2 mg with 40 μL catalyst ink.

The H₂O₂ production reaction (HPR) was performed in an H-cell with a glass filter, with a Fe-CNT electrode as the working electrode, a Pt wire as the counter electrode, and a Hg/HgO reference electrode in 1 M NaOH solution. Prior to the measurements, the electrolyte was purged with O₂ gas for 15 min. Then, the electrocatalytic performance of the Fe-CNT electrode was investigated in 1 M NaOH solution and continuous O₂ gas bubbling via CV and linear scan voltammetry (LSV) at 10 mV/s, and chronoamperometry (CA) at different potentials (-0.2, -0.3, -0.4, -0.5 V vs. Hg/HgO). All potentials measured against Hg/HgO were converted to the reversible hydrogen electrode (RHE) scale using $E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098 \ V + 0.059 \times \text{pH}$, where pH values of solutions were determined by the Orion 810 BNUWP ROSS Ultra pH electrode (13.44 for 1M NaOH solution).

To determine the Faradaic efficiency (FE) of the alkaline HPR, the concentration of the H₂O₂ generated from CA was quantified by the colorimetric titration with ceric sulfate. Specifically, 0.4 mM Ce(SO₄)₂ solution was first prepared by dissolving Ce(SO₄)₂ (Sigma Aldrich) in 0.5 M H₂SO₄. And the calibration curve was constructed by measuring the UV-Vis spectroscopy of Ce(SO₄)₂ solutions using a Cary 50 SCAN spectrometer with different concentrations. The wavelength used for the measurement is 319 nm.

The sample solution containing H₂O₂ with a proper volume was added into 5.0 mL 0.4 mM Ce(SO₄)₂ solution and measured by the UV-Vis spectroscopy. Then, the remained concentration of Ce(SO₄)₂ solution could be determined using the calibration curve. The concentration of H₂O₂ could be determined by the following equations:

$$2\text{Ce}^{4+} + \text{H}_2\text{O}_2 \rightarrow 2\text{Ce}^{3+} + 2\text{H}^+ + \text{O}_2$$

$$[\text{H}_2\text{O}_2] \ (\text{mM}) = \frac{V_1 \times [\text{Ce}^{4+}] - (V_1 + \Delta V) \times [\text{Ce}^{4+}, \text{detected}]}{\Delta V \times 2} \ (S5)$$

where $V_1$, $\Delta V$, $[\text{Ce}^{4+}]$ and $[\text{Ce}^{4+}, \text{detected}]$ are the original volume of 0.4 mM Ce⁴⁺ standard solution, the volume of added H₂O₂ sample solution, the concentration of standard Ce⁴⁺ solution, and the detected concentration of Ce⁴⁺ solution after adding H₂O₂ sample, respectively. In this experiment, $V_1$ was 5.0 mL and $[\text{Ce}^{4+}]$ was 0.4 mM.

The FE of H₂O₂ production reaction was then calculated based on the concentration of
detected $\text{H}_2\text{O}_2$ and input charge using the following equation:

$$\text{FE (\%)} = \frac{Q \text{ for } \text{H}_2\text{O}_2 \text{ production}}{Q_{\text{input}}} \times 100 = \frac{[\text{H}_2\text{O}_2] \times V \times 2 \times 96485}{Q_{\text{input}}} \times 100 \quad (S6)$$

where $V$, $[\text{H}_2\text{O}_2]$, and $Q_{\text{input}}$ are the volume of the solution, the concentration of produced $\text{H}_2\text{O}_2$ and the input charge during the electrosynthesis, respectively.

**Demonstration of ion-balanced ModES process enabled by RR**

To demonstrate the co-production of $\text{H}_2\text{O}_2$ and $\text{NaClO}$ in an ion-balanced ModES system, two electrochemical cells, the $\text{H}_2\text{O}_2$ cell (Cell$_{\text{H}_2\text{O}_2}$) containing 30 mL 1 M $\text{NaOH}$ solution, and the $\text{NaClO}$ cell (Cell$_{\text{NaClO}}$) with 30 mL of 1 M $\text{NaCl}$ solution were used. A Ni(OH)$_2$ RR electrode with the size of $2 \times 3$ cm$^2$ and an active materials loading of 59.6 mg (passing 45 Coulombs per ModES cycle) was used as the counter electrode in both cells. In Cell$_{\text{H}_2\text{O}_2}$, the Fe-CNT electrode (catalyst loading around 0.2 mg) and a Hg/HgO electrode were used as the working electrode and reference electrode. The electrolyte was continuously bubbled with $\text{O}_2$ gas to ensure the $\text{O}_2$ saturation. In the Cell$_{\text{NaClO}}$, a DSA electrode (1$\times$3 cm$^2$) and a SCE were used as the working electrode and the reference electrode, respectively. All ModES processes were measured under a constant current of 60 mA.

As illustrated in Figure S17, in the Cell$_{\text{H}_2\text{O}_2}$, the RR oxidation from RR$_{\text{red}}$ to RR$_{\text{ox}}$ consumed $\text{OH}^-$, and the oxygen reduction generated $\text{H}_2\text{O}_2$ and $\text{OH}^-$. After passing 45 Coulombs, the RR$_{\text{ox}}$ electrode was taken out of the Cell$_{\text{H}_2\text{O}_2}$, washed with 1 M $\text{NaCl}$ solution to remove the residual electrolyte, and then moved to the Cell$_{\text{NaClO}}$. In the Cell$_{\text{NaClO}}$, the RR$_{\text{ox}}$ was reduced to RR$_{\text{red}}$ and generated $\text{OH}^-$ until -0.14 V vs. SCE (0 V vs. Hg/HgO), and $\text{Cl}^-$ was oxidized on the DSA electrode to produce $\text{ClO}^-$. During the ModES co-production, the RR electrode effectively transported the $\text{OH}^-$ formed from HPR to balance the $\text{OH}^-$-consuming HCR, contributing to the ion-balanced co-production without appreciable pH swing. The RR electrode’s potential was also monitored to calculate the total cell voltage ($E_{\text{cell}}$), i.e., the potential difference between the RR and the Fe-CNT electrode or the DSA electrode. During these ModES cycles, the capacity of the RR electrode was controlled by the potential and capacity restrictions to make sure the RR electrode was operated within the desired potential windows. Furthermore, the pH shift in the Cell$_{\text{NaClO}}$ was recorded during the ModES cycles. The initial pH of 1 M $\text{NaCl}$ solution was
measured when the DSA electrode, the RR electrode, and the SCE electrode were immersed in the solution before HCR and the final pH of this solution was measured after the HCR process.

The concentrations of the produced H$_2$O$_2$ and NaClO were measured following the procedures described above. Based on the product concentrations, the Faradaic efficiencies were calculated according to the following equations:

\[
FE(\%)_{\text{H}_2\text{O}_2} = \frac{Q \text{ for } \text{H}_2\text{O}_2 \text{ production}}{Q_{\text{passing, RR}}} \times 100 = \frac{[\text{H}_2\text{O}_2] \times V \times 2 \times 96485}{Q_{\text{passing, RR}}} \times 100 \quad (S7)
\]

\[
FE(\%)_{\text{ClO}^-} = \frac{Q \text{ for } [\text{ClO}^-] \text{ production}}{Q_{\text{passing, RR}}} \times 100 = \frac{[\text{ClO}^-] \times V \times 2 \times 96485}{Q_{\text{passing, RR}}} \times 100 \quad (S8)
\]

where the $Q_{\text{passing, RR}}$ is the charge passing through the RR electrode in the Cell$_{\text{H}_2\text{O}_2}$ and the Cell$_{\text{NaClO}}$.

For the larger scale ModES reaction in a 60 mL solution, a Ni(OH)$_2$ RR electrode with an area of 2 × 3 cm$^2$ and an active materials loading of 136.9 mg (passing 90 Coulombs per ModES cycle) was used as the counter electrode in both cells. In the Cell$_{\text{H}_2\text{O}_2}$, two Fe-CNT electrodes (mass loading of each electrode around 0.2 mg) were used back-to-back as the working electrode together with the Hg/HgO reference electrode (Figure S18). The electrolyte was continuously bubbled with O$_2$ gas to ensure the O$_2$ saturation. In the Cell$_{\text{NaClO}}$, a DSA electrode (1×3 cm$^2$) and a SCE were used as the working electrode and the reference electrode. The operations during the ModES cycles, the calculation of products’ concentrations, and FE calculation followed the same procedures for the small-scale production.
2. Chemical stability of H$_2$O$_2$ mixed with Ni(OH)$_2$ powder

Figure S1. The detections of the remained H$_2$O$_2$ in 5 mL 300 ppm H$_2$O$_2$ solution mixed with 10 mg Ni(OH)$_2$ using test strips. (a) The photograph of the H$_2$O$_2$ test strips. (b) The H$_2$O$_2$ detection using test strips on 300 ppm H$_2$O$_2$ solution after 24 h (red-dashed line) and 300 ppm H$_2$O$_2$ solution mixed with 10 mg Ni(OH)$_2$ after 24 h (purple-dashed line). Tests were conducted in solutions with a 1:30 dilution (~10 ppm). (c) The H$_2$O$_2$ detection using test strips on 300 ppm H$_2$O$_2$ solution after 72 h (red-dashed line) and 300 ppm H$_2$O$_2$ solution mixed with 10 mg Ni(OH)$_2$ after 72 h (blue-dashed line). Tests were conducted in solutions with a 1:60 dilution (~5 ppm).
3. XRD of the as-synthesized Ni(OH)₂ powder and Ni(OH)₂ electrodes

Figure S2. Powder X-ray diffraction (PXRD) pattern of (a) the as-synthesized Ni(OH)₂ powder and (b) Ni(OH)₂ electrodes. For the as-synthesized Ni(OH)₂ powder, the characteristic (003), (101), and (015) diffraction peaks match well with the standard pattern of α-Ni(OH)₂ (JCPDS no. 38-0715). For Ni(OH)₂ electrodes after activation or 50-cycle ModES processes, the characteristic (001), (100), (011), and (012) diffraction peaks match well with the standard pattern of β-Ni(OH)₂ (JCPDS no. 73-1520).
4. Electrochemical characterizations of the Ni(OH)$_2$ RR electrodes

**Figure S3.** Photograph of a Ni(OH)$_2$ RR electrode. The size of this electrode is $2.0 \times 3.0$ cm$^2$ based on the active material (black area).

**Figure S4.** The activation process of the Ni(OH)$_2$ electrode. 20-cycle galvanostatic charge-discharge (GCD) tests at 1C rate were run as the activation process for all Ni(OH)$_2$ electrodes before other electrochemical measurements. The capacity and Coulombic efficiency (CE) are shown as the black and red dots, respectively. The 1 C rate is defined as 289 mA g$^{-1}$ based on the theoretical capacity (289 mAh g$^{-1}$) of Ni(OH)$_2$. 

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Figure S5. The rate performance and Coulombic efficiency (CE) of the Ni(OH)$_2$ electrode in 1 M NaOH solution. The capacity and CE are shown as the black and red dots, respectively. The nC rate means that the discharge current will discharge the entire battery in 1/n hours. Since Ni(OH)$_2$’s theoretical capacity is 289 mAh g$^{-1}$, the 1 C rate is 289 mA g$^{-1}$, and the 2 C rate is 578 mA g$^{-1}$. 
Figure S6. Cycling performance of the Ni(OH)$_2$ electrodes at (a) 1 C rate, (b) 2 C rate, and (c) 10 C rate in 1 M NaOH solution, corresponding to 289 mA g$^{-1}$, 578 mA g$^{-1}$, and 2.89 A g$^{-1}$. The decay rate per cycle was 0.28 %, 0.19 %, and 0.064 % at 1 C rate, 2 C rate, and 10 C rate, respectively.
Figure S7. Galvanostatic charge-discharge (GCD) curves of the Ni(OH)$_2$ electrodes in various solutions at 10 C rate (2.89 A g$^{-1}$). GCD curves of the Ni(OH)$_2$ electrodes in (a) 1 M NaOH solution (0.1 V to 0.7 V vs. SHE) and (b) 1 M Na$_2$SO$_4$ solution (0.1 V to 0.85 V vs. SHE). (c) Galvanostatic charge curve of the Ni(OH)$_2$ electrode in 1 M NaOH solution (0.1 V to 0.7 V vs. SHE) and its galvanostatic discharge curve in 1 M NaCl solution (discharge to 0.1V vs. SHE). (d) Galvanostatic charge curve of the Ni(OH)$_2$ electrode in 1 M NaOH solution (0.1 V to 0.7 V vs. SHE) and its galvanostatic discharge curve in 1 M Na$_2$SO$_4$ solution (discharge to 0.1V vs. SHE). Capacity is normalized based on the charging capacity in 1 M NaOH solution.
**Figure S8.** Galvanostatic charge-discharge (GCD) curves of the Ni(OH)$_2$ electrodes in weak alkaline solutions (pH 9 and 10) at 10 C rate (2.89 A g$^{-1}$). GCD curves of the Ni(OH)$_2$ electrode in 1 M NaCl solution with a buffered pH of (a) 9 or (b) 10. Capacity is normalized based on the charging capacity in 1 M NaOH solution.

**Table S1.** Capacity of the Ni(OH)$_2$ electrodes at 10 C rate in various solutions (The capacity was normalized based on the charging capacity in 1 M NaOH solution).

| Number | Charge step | Normalized $C_{\text{charging}}$ (%) | Discharge step | Normalized $C_{\text{discharging}}$ (%) | Coulombic efficiency (%) |
|--------|-------------|--------------------------------------|----------------|----------------------------------------|--------------------------|
| 1      | 1 M NaOH    | 100.0                                | 1 M NaOH       | 99.1                                   | 99.1                     |
| 2      | 1 M Na$_2$SO$_4$ | 0.12                            | 1 M Na$_2$SO$_4$ | 0.16                                  | > 100                    |
| 3      | 1 M NaCl, pH = 9 | 0.42                            | 1 M NaCl, pH = 9 | 0.45                                  | > 100                    |
| 4      | 1 M NaCl, pH = 10 | 1.19                            | 1 M NaCl, pH = 10 | 1.16                                  | 97.5                     |
| 5      | 1 M NaOH    | 91.0                                 | 1 M Na$_2$SO$_4$ | 88.7                                   | 97.5                     |
| 6      | 1 M NaOH    | 97.9                                 | 1 M NaCl        | 92.4                                   | 94.4                     |
5. Hydroxide-ion balancing ability of the Ni(OH)$_2$ RR

**Table S2.** The pH swing and corresponding passing charge during GCD tests of the Ni(OH)$_2$ electrode (oxygen evolution reaction written as OER and hypochlorite generation reaction written as HCR).

| Reactions$^{[a]}$ | Step | Electrolyte | Cell | pH        | Q (C)$^{[b]}$ |
|------------------|------|-------------|------|-----------|--------------|
| H-cell: RR       | Charge | 1 M NaOH     | ---  | ---       | 2.9          |
| reduction and    | Discharge | 1 M Na$_2$SO$_4$ | H-cell (RR side) | 4.80 to 11.04 | 3.1          |
| OER              | Discharge | 1 M Na$_2$SO$_4$ | H-cell (OER side) | 10.82 to 5.70 | 3.1          |
| Beaker-type cell:| Charge  | 1 M NaOH     | ---  | ---       | 2.9          |
| RR reduction and | Discharge | 1 M Na$_2$SO$_4$ | Beaker-type cell | 10.94 to 10.82 | 3.1          |
| OER              |         |             |      |           |              |
| H-cell: RR       | Charge  | 1 M NaOH     | ---  | ---       | 2.7          |
| reduction and    | Discharge | 1 M NaCl     | H-cell (RR side) | 5.18 to 11.01 | 2.8          |
| HCR              | Discharge | 1 M NaCl     | H-cell (HCR side) | 5.16 to 3.08 | 2.8          |
| Beaker-type cell:| Charge  | 1 M NaOH     | ---  | ---       | 2.9          |
| RR reduction and | Discharge | 1 M NaCl     | Beaker-type cell | 5.36 to 7.36 | 3.1          |
| HCR              |         |             |      |           |              |

$^{[a]}$ The Ni(OH)$_2$ electrode was charged in 1 M NaOH solution before the reduction process. The volume of solutions in both beaker-type cell and H-cell was 15 mL.

$^{[b]}$ The CE above 100 % may result from the various potential windows in different solutions. In alkaline solution, all Ni(OH)$_2$ electrodes were charged to 0.7 V vs. Hg/HgO at 10 C rate. And the RR electrodes were discharged to -0.14 V vs. SCE (0 V vs. Hg/HgO) in neutral solution.
6. HCR process using DSA electrodes

**Figure S9.** The effect of pH on the dissociation of hypochlorous acid.\(^8\) The HCR production will obtain a mixture of HClO and ClO\(^-\) due to the partial dissociation of HClO in the aqueous solution. The oxidation of Cl\(^-\) prefers chlorate product rather than ClO\(^-\) when the pH is around 6.5 with a high temperature. When pH is above 8, most chlorine presents as ClO\(^-\) in the solution with less reactive activity and lower decay rate. In the on-site seawater hypochlorite cells, the solution pH is typically around pH = 9 to minimize the chlorate formation.\(^8,9\)

**Figure S10.** Electrochemical configurations of HPR and HCR in conventional electrolysis. (a) HCR process was conducted in an undivided cell to minimize the pH shift. (b) HPR process was conducted in a H-cell with a glass frit in O\(_2\)-saturated 1 M NaOH solution.
Figure S11. Cyclic voltammetry (CV), Chronoamperometry (CA) curves and potential-dependent Faradaic efficiency (FE) of the DSA electrode in 1 M NaCl solution with pH = 6.0 (a-c), 8.5 (d-f), 11.0 (g-i), and 13.3 (j-l), respectively. The CV were measured at a scan rate of 10 mV s⁻¹. The 1 M NaCl solutions with various pH were prepared by adding NaOH or HCl solution. The onset potential in pH ranging from 6.0 to 8.5 decreased slowly, while the onset potential in pH 13.3 dropped to 600 mV, indicating the OER was the major reaction in the alkaline solution.
7. HPR process using Fe-CNT catalysts

**Figure S12.** TEM images of carbon nanotube (CNT) and Fe-decorated carbon nanotube (Fe-CNT) catalysts. CNT catalysts with scale bar: (a) 100 nm and (b) 20 nm; Fe-CNT catalysts with scale bar: (c) 100 nm and (d) 20 nm.

**Figure S13.** XPS survey spectra of the CNT and Fe-decorated CNT. Only C (284.8 eV) and O (532.2 eV) elements were detected. Insert is the atomic content table.
Figure S14. Electrochemical characterizations of the CNT electrode. (a) Linear scanning voltammetry (LSV) curve of the CNT electrode at 10 mV s\(^{-1}\) and potential-dependent FE of HPR in O\(_2\)-saturated 1 M NaOH solution. (b) CA curves of the CNT electrode in O\(_2\)-saturated 1 M NaOH solution at various applied potentials. The mass loading of the CNT catalyst was 0.2 mg.

Figure S15. Absorption spectra of (a) standard solutions of Ce(SO\(_4\))\(_2\) (up to 0.4 mM) in 0.5 M H\(_2\)SO\(_4\) and (b) the calibration curve at the peak wavelength of 319 nm.
Figure S16. Comparison of Fe-CNT and CNT electrodes during ORR in O₂-saturated 1 M NaOH solution. (a) CV and (b) potential-dependent FE of CNT and Fe-CNT electrodes to produce H₂O₂. The mass loading of both electrodes was 0.2 mg.

8. Operation of Ion-balanced ModES processes using a RR

Figure S17. Schematic of the operations of the OH⁻-balanced ModES system. The HPR process was conducted first with the RR oxidation. Then the RR electrode was washed by 1 M NaCl solution with a pH of 8.5 and reduced in the CellNaClO, pairing with the HCR process to finish one-cycle of ModES. After a typical ModES cycle, the RR electrode would be washed with 1 M NaOH solution and used again for HPR for continuous production.
**Figure S18.** Schematic of the ModES processes of HPR and HCR in 30 mL and 60 mL solutions. For ModES processes in 60 mL solutions, two Fe-CNT electrodes were assembled back-to-back to minimize the current fluctuation arising from the oxygen gas bubbles. One Fe-CNT electrode was used during ModES processes in 30 mL solutions.

**9. H$_2$O$_2$ decomposition during ModES process**

**Figure S19.** The accumulation of H$_2$O$_2$ in O$_2$-saturated 1 M NaOH solution during the ModES
process. The theoretical concentration of produced H₂O₂ and corresponding passing charges were controlled by the RR electrodes with different mass loadings of 22 mg, 60 mg, and 116 mg.

Figure S20. Electrochemical oxidation of H₂O₂ by the Ni(OH)₂ electrodes. (a) CV curves of the Ni(OH)₂ electrode in 1 M NaOH solution and 1 M NaOH solution containing 300 ppm H₂O₂. (b) The iR-correct LSV of the Ni(OH)₂ electrode in 1 M NaOH solution with different concentrations of H₂O₂ (0 ppm, 300 ppm, 600 ppm, and 900 ppm). (c) GCD curves of the Ni(OH)₂ electrode in 1 M NaOH solution containing 300 ppm H₂O₂. The current is 10 C rate (2.89 A g⁻¹).
10. Ion-balanced ModES processes to co-produce H₂O₂ and NaClO

Figure S21. Electrochemical performance of the RR electrode and catalytic electrodes in the small-scale ModES processes (30 mL solutions). (a) CV of a Ni(OH)₂ RR in 1 M NaOH solution and LSV of HPR in 1 M NaOH solution and HCR in 1 M NaCl with a pH of 8.5. (b) Potential of
a Ni(OH)$_2$ RR paired with HPR (red curves) and HCR (black curves) over ten ModES cycles. (c) Potential of HPR on the Fe-CNT electrode in 1 M NaOH solution (red curves) and HCR on the DSA electrode in 1 M NaCl solution (black curves). (d) Corresponding cell voltages over ten ModES cycles (red curves for the H$_2$O$_2$ cell and black curves for the NaClO cell). (e) Modular co-production of H$_2$O$_2$ and NaClO at 30 mL.

**Figure S22.** Electrochemical performance of the RR electrode and catalytic electrodes in the large-scale ModES processes (60 mL solutions). (a) Potential of a Ni(OH)$_2$ RR paired with HPR (red curves) and HCR (black curves) over five ModES cycles. (b) Potential of HPR on Fe-CNT electrode in 1 M NaOH solution (red curves) and HCR on DSA electrode in 1 M NaCl solution (black curves). (c) Corresponding cell voltages over five ModES cycles (red curves for the H$_2$O$_2$ cell and black curves for the NaClO cell). (d) CE, VE, and pH shift in the NaClO cell over five ModES cycles.
Figure S23. Large-scale ion-balanced ModES processes to produce H$_2$O$_2$ and NaClO. (a) The average potential of a Ni(OH)$_2$ RR ($E_{\text{RR}}$, top panel) and the corresponding average cell voltages ($V_{\text{cell}}$, bottom panel) of Cell$_{\text{H}_2\text{O}_2}$ and Cell$_{\text{NaClO}}$ in five large-scale ModES production. (b) Modular processes to produce H$_2$O$_2$ and NaClO in 60 mL solution, showing the product concentration up to 251 ppm (red column) and 481 ppm (grey column), as well as the FE (red dots and black dots) for each ModES cycle.
Figure S24. 50-cycle ion-balanced ModES processes to produce H$_2$O$_2$ and NaClO. (a) CE, VE, and pH shift in the NaClO cell over 50 ModES cycles. (b) The utilization of the Ni(OH)$_2$ RR. (c) The average potentials of the Ni(OH)$_2$ RR ($E_{RR}$, top panel) and the corresponding average cell voltages ($V_{cell}$, bottom panel) of Cell$_{H_2O_2}$ and Cell$_{NaClO}$. 
**Figure S25.** Potential of the Ni(OH)$_2$ RR paired with HPR (red curves) and HCR (black curves) over 50 ModES cycles.

**Table S3.** The utilization of Ni(OH)$_2$ RR electrodes during ModES processes.

| Cycle | H$_2$O$_2$ production (%) | NaClO production (%) | Cycle | H$_2$O$_2$ production (%) | NaClO production (%) | Cycle | H$_2$O$_2$ production (%) | NaClO production (%) |
|-------|---------------------------|----------------------|-------|---------------------------|----------------------|-------|---------------------------|----------------------|
| 1     | 96.6                      | 82.2                 | 1     | 95.5                      | 87.9                 | 1     | 87.0                      | 86.0                 |
| 2     | 96.6                      | 96.6                 | 5     | 95.5                      | 90.4                 | 2     | 87.0                      | 82.0                 |
| 3     | 96.6                      | 91.5                 | 10    | 95.5                      | 92.6                 | 3     | 87.0                      | 75.2                 |
| 4     | 96.6                      | 95.1                 | 15    | 95.5                      | 92.4                 | 4     | 87.0                      | 82.3                 |
| 5     | 96.6                      | 86.9                 | 20    | 95.5                      | 89.8                 | 5     | 87.0                      | 80.7                 |
| 6     | 96.6                      | 84.8                 | 25    | 95.5                      | 84.9                 |       |                           |                      |
| 7     | 96.6                      | 79.7                 | 30    | 95.5                      | 91.5                 |       |                           |                      |
| 8     | 96.6                      | 84.5                 | 35    | 95.5                      | 89.8                 |       |                           |                      |
| 9     | 96.6                      | 83.0                 | 40    | 95.5                      | 90.2                 |       |                           |                      |
| 10    | 96.6                      | 84.1                 | 45    | 95.5                      | 93.0                 |       |                           |                      |

[a] The capacity of this Ni(OH)$_2$ RR is 46.6 Coulombs (59.6 mg, 217 mAh g$^{-1}$) at 60 mA in 1 M NaOH solution. It passes 45 Coulombs during the H$_2$O$_2$ production for each cycle.

[b] The capacity of this Ni(OH)$_2$ RR is 47.1 Coulombs (61.0 mg, 214 mAh g$^{-1}$) at 60 mA in 1 M NaOH solution. It passes 45 Coulombs during the H$_2$O$_2$ production for each cycle.
The capacity of this Ni(OH)2 RR is 103.5 Coulombs (136.9 mg, 210 mAh g⁻¹) at 60 mA in 1 M NaOH solution. It passes 90 Coulombs during the H₂O₂ production for each cycle.

Note: We used three different RR electrodes for the above ModES processes. For each ModES cycle, we performed the H₂O₂ production and the RR oxidation in 1 M NaOH solution. The NaClO production paired with the RR reduction was performed in 1 M NaCl solution with a pH of 8.5. Given the difficulty to measure the exact capacity and the state of charge (SOC) of the RR electrodes in the above conditions, it is hard to use the same utilization of the RR electrodes in the H₂O₂ production and NaClO production. To effectively control the initial SOC of the RR electrodes, we reduced the Ni(OH)₂ electrodes to -0.14 V vs. SCE (0 V vs. Hg/HgO) in each ModES cycle.

11. References cited in the Supporting Information:

1. Jiang, H.; Zhao, T.; Li, C.; Ma, J., Hierarchical self-assembly of ultrathin nickel hydroxide nanoflakes for high-performance supercapacitors. *J. Mater. Chem.* **2011**, *21*.

2. Jiang, K.; Back, S.; Akey, A. J.; Xia, C.; Hu, Y.; Liang, W.; Schaak, D.; Stavitski, E.; Norskov, J. K.; Siahrostami, S.; Wang, H., Highly selective oxygen reduction to hydrogen peroxide on transition metal single atom coordination. *Nat. Commun.* **2019**, *10*, 3997.

3. 4500-Cl- CHLORIDE. In *Standard Methods For the Examination of Water and Wastewater*, 23rd ed.; E.W. Rice, R. B. B., A.D. Eaton, Ed. American Public Health Association: Washington, 2018; pp 405-418.

4. Sheng, H.; Hermes, E. D.; Yang, X.; Ying, D.; Janes, A. N.; Li, W.; Schmidt, J. R.; Jin, S., Electrocatalytic Production of H₂O₂ by Selective Oxygen Reduction Using Earth-Abundant Cobalt Pyrite (CoS₂). *ACS Catal.* **2019**, *9*, 8433-8442.

5. Sheng, H.; Janes, A. N.; Ross, R. D.; Kaiman, D.; Huang, J.; Song, B.; Schmidt, J. R.; Jin, S., Stable and selective electrosynthesis of hydrogen peroxide and the electro-Fenton process on CoSe₂ polymorph catalysts. *Energy Environ. Sci.* **2020**, *13*, 4189-4203.

6. Lu, Z.; Chen, G.; Siahrostami, S.; Chen, Z.; Liu, K.; Xie, J.; Liao, L.; Wu, T.; Lin, D.; Liu, Y.; Jaramillo, T. F.; Norskov, J. K.; Cui, Y., High-efficiency oxygen reduction to hydrogen peroxide catalysed by oxidized carbon materials. *Nat. Catal.* **2018**, *1*, 156-162.

7. Bonnick, P.; Dahn, J. R., A Simple Coin Cell Design for Testing Rechargeable Zinc-Air or Alkaline Battery Systems. *J. Electrochem. Soc.* **2012**, *159*, A981-A989.
8. Matousek, R., Hypochlorite Synthesis Cells and Technology, Sea Water. In *Encyclopedia of Applied Electrochemistry*, 2014 ed.; Kreysa, G.; Ota, K.-i.; Savinell, R. F., Eds. Springer New York: New York, 2014; pp 1066-1070.

9. Corporation, B. V., Hypochlorination—Sodium Hypochlorite. In *White's Handbook of Chlorination and Alternative Disinfectants*, 5th ed.; Dominic M. Desiderio, N. M. M. N., Ed. John Wiley & Sons, Inc: New Jersey, 2009; pp 452-527.