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## **Supplemental Information**

## Modular Electrochemical Synthesis Using a Redox

### **Reservoir Paired with Independent Half-Reactions**

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### Supplemental Information

#### А C Е G aNiH NIH nm В Н D F Element Element Atomic ratio % Element Atomic ratio % Atomic ratio % Element Atomic ratio % С 28.05 С 39.52 С 33.21 С 31.63 38.09 34.88 Ν Ν Ν 35.50 Ν 36.99 0 9.73 0 0 12.22 14.76 0 15.96 Na 11.98 Na 8.39 Na 9.31 Na 9.24 Fe 3.34 Fe Fe 4.95 3.37 Fe 3 Ni 3.18 Ni 4.71 4.14 Ni 3.84 Ni

#### **Supplemental Experimental Procedures**

#### Figure S1. Characterization of the different sodium nickel hexacyanoferrate (NaNiHCF) samples.

(A, C, E, G) SEM images and the corresponding (B, D, F, H) EDS elemental analyses of various NaNiHCF-x (n<sub>Ni</sub>: n<sub>cittate</sub>

=1: x) samples. The size of the synthesized NaNiHCF crystals increased with the citrate ratio used in the synthesis.



# Figure S2. Comparison of the PXRD patterns collected on various NaNiHCF-*x* samples with the standard pattern of cubic Prussian blue crystal (JCPDS No. 52-1907).

The obvious doublet diffraction peaks at (220), (420), (440) and (620) are observed for various NaNiHCF-*x* sample, indicating the rhombohedral structure of these samples.



Figure S3. Thermogravimetric analysis (TGA) of various NaNiHCF-x samples.

(A) NaNiHCF-1. (B) NaNiHCF-5. (C) NaNiHCF-10. (D) NaNiHCF-15. The TGA tests were carried out under  $N_2$  atmosphere at a ramp rate of 10 °C/min. The water contents in these various samples can be calculated based on these TGA results, as labeled in each panel for the first weightloss step.

**Table S1.** Weight percentages of metal elements and water content in various NaNiHCF-x samples. These values were

 calculated from the ICP-OES and TGA results.

| sample     | Na     | Ni     | Fe     | H <sub>2</sub> O |
|------------|--------|--------|--------|------------------|
| NaNiHCF-1  | 22.78% | 34.95% | 24.67% | 17.60%           |
| NaNiHCF-5  | 27.19% | 31.18% | 27.69% | 13.93%           |
| NaNiHCF-10 | 25.60% | 39.75% | 24.25% | 10.39%           |
| NaNiHCF-15 | 24.65% | 41.08% | 23.21% | 11.06%           |



# Figure S4. XRD patterns of the NaNiHCF-10 RR electrode (with Ti current collector) at different state of the redox reservoir (SOR).

Before oxidation (0% SOR), the NaNiHCF-10 RR electrode had rhombohedral crystal structure. After this RR electrode was fully oxidized (100% SOR), its crystal phase changed to cubic. The peaks marked with "\*" are attributed to the signal from the Ti current collector.



Figure S5. Stability measurements of various NaNiHCF-x electrodes.

Comparison of the cycling performance of various NaNiHCF-x electrodes in 1.7 M Na<sub>2</sub>SO<sub>4</sub> electrolyte with a cycling rate of 100 mAg<sup>-1</sup>. The capacity decay rates of these electrodes are summarized in Table S2 (also see **Table S2**).



Figure S6. Cycling performance of NaNiHCF-10 RR electrode.

Energy efficiency of NaNiHCF-10 electrode cycled in 1.7 M Na<sub>2</sub>SO<sub>4</sub> electrolyte with a cycling rate of 100 mA g<sup>-1</sup>.

**Table S2.** Comparison of the stability of various NaNiHCF-x electrodes under the same measurement conditions. At least

 3 electrodes were tested for each case to obtain average experimental values. Here, by tuning the ratio between Ni<sup>2+</sup> and

 sodium citrate(1: x) during the co-precipitation synthesis, we can obtain the various NaNiHCF crystals accordingly.

| Electrode  | Current density<br>(mA/g) | Capacity<br>(mAh/g) | Electrolyte                                      | Decay rate |         |
|------------|---------------------------|---------------------|--|------------|---------|
|            |                           |                     |  | %/day      | %/cycle |
| NaNiHCF-1  | 100                       | 55-65               | 1.7 M Na <sub>2</sub> SO <sub>4</sub>            | <0.60%     | <0.03%  |
| NaNiHCF-5  | 100                       | 60-70               | 1.7 M Na <sub>2</sub> SO <sub>4</sub>            | <0.73%     | <0.04%  |
| NaNiHCF-10 | 100                       | 65-70               | 1.7 M Na <sub>2</sub> SO <sub>4</sub>            | <0.55%     | <0.04%  |
| NaNiHCF-15 | 100                       | 65-70               | $1.7 \mathrm{M} \mathrm{Na}_{2} \mathrm{SO}_{4}$ | <0.92%     | <0.05%  |



Figure S7. Electrochemical properties of the NaNiHCF-10 RR electrode tested at different current rates. Capability of the NaNiHCF-10 RR electrode cycled at various rates of 0.1, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 A g<sup>-1</sup> in 1.7 M Na<sub>2</sub>SO<sub>4</sub> electrolyte. For each rate, 10 galvanostatic cycles were conducted with the same cut-off potentials of 0.2 and 1.0  $V_{SHE}$ .



Figure S8. Electrochemical properties of three NaNiHCF-10 electrodes connected in parallel.

Specific capacity and Coulombic efficiency of three NaNiHCF-10 RR electrodes connected in parallel cycled at 100 mA  $g^{-1}$  from 0.2 to 1.0 V<sub>SHE</sub> in 1.7 M Na<sub>2</sub>SO<sub>4</sub> electrolyte for 120 cycles. Inset, the schematic illustration of the three RR electrodes (1×1 cm<sup>2</sup>) connected in parallel. The capacity decay rate of NaNiHCF-10 electrodes connected in parallel was 0.01%/cycle(0.18%/day).



Figure S9. Characterization of the commercial carbon felt (treated in air at 400 °C for 24 h) used as the working

electrode to produce H<sub>2</sub>O<sub>2</sub> in 1.7 M Na<sub>2</sub>SO<sub>4</sub> electrolyte.

- (A) Photograph of the carbon felt electrode  $(2 \times 3 \text{ cm}^2)$ .
- (B) SEM image of the carbon felt electrode under high magnification.



Figure S10. Comparison of the XPS spectra collected on the pristine and the treated carbon felt.

(A) O 1s. (B) C 1s spectra. Treating the carbon felt can introduce or increase some functional groups, such as C-O-H, C-O-C, which enhances its catalytic performance for oxygen reduction reaction<sup>1</sup>.



Figure S11. Investigation of electrochemical H<sub>2</sub>O<sub>2</sub> production in conventional divided cells in a neutral electrolyte (1.7 M Na<sub>2</sub>SO<sub>4</sub>).

(A) Cyclic voltammetry (CV) curve of the treated carbon felt electrode scanned at  $10 \text{ mV s}^{-1}$  for  $H_2O_2$  production in 1.7 M

 $Na_2SO_4\ solution\ purged\ with\ O_2\ gas.$ 

(B) Fast preliminary detection of the  $H_2O_2$  produced under chronoamperometry for 5 min at 0  $V_{SHE}$  in 1.7 M Na<sub>2</sub>SO<sub>4</sub> electrolyte using  $H_2O_2$  testing strips.

#### Supplemental experimental procedures: detection of produced H<sub>2</sub>O<sub>2</sub>

The concentration of the electrochemically produced  $H_2O_2$  in 1.7 MNa<sub>2</sub>SO<sub>4</sub> electrolyte was determined by the ceric sulfate titration process based on the following reaction<sup>1</sup>:

$$2Ce^{4+} + H_2O_2 \rightarrow 2Ce^{3+} + 2H^+ + O_2$$
 (S1)

The chromogenic reagent was prepared by dissolving  $Ce(SO_4)_2$  (0.4 mM, Sigma Aldrich) in 0.5 M H<sub>2</sub>SO<sub>4</sub>. UV/Vis spectroscopy (Cary 50 SCAN) of the solutions was performed to determine the concentration of  $Ce^{4+}$ , which has an absorbance peak at 319 nm in contrast to the colorless  $Ce^{3+}$ . Thus, the reduction of  $Ce^{4+}$  to  $Ce^{3+}$  by H<sub>2</sub>O<sub>2</sub> could lead to a decrease in the absorbance peak intensity (see Figure S12). Accordingly, the concentration of produced H<sub>2</sub>O<sub>2</sub> (i.e., [H<sub>2</sub>O<sub>2</sub>]) can be calculated based on the following equations:<sup>1,2</sup>

$$\frac{Abs_{before}}{[Ce_{before}^{4+}]} = \frac{Abs_{affer}}{[Ce_{affer}^{4+}]}$$
(S2)

$$[H_2 O_2] (mM) = \frac{V_{before} \times [Ce_{before}^{4+}] \cdot (V_{before} + \Delta V) \times [Ce_{after}^{4+}]}{\Delta V \times 2}$$
(S3)

where the  $[Ce_{before}^{4+}]$ ,  $[Ce_{after}^{4+}]$ ,  $V_{before}$  and  $\Delta V$  are the concentration of  $Ce^{4+}$  ion before and after adding the  $H_2O_2$  solution, the original volume of the 0.4 mM Ce<sup>4+</sup> standard solution and the added  $H_2O_2$  solution.



Figure S12. Ceric sulfate titration followed by UV-Vis spectroscopy for determining the concentration of the produced H<sub>2</sub>O<sub>2</sub>.

UV-vis spectra of 5 mL 0.4 mM Ce(SO<sub>4</sub>)<sub>2</sub> solution before and after adding 1 mL 1.7 M Na<sub>2</sub>SO<sub>4</sub> solution containing ~0.4 mM H<sub>2</sub>O<sub>2</sub>, which was produced on treated carbon felt electrode. The change of the peak intensity can be used to calculate the exact concentration of the produced H<sub>2</sub>O<sub>2</sub>.



#### Figure S13. Characterization of the DoSi wafer.

- (A) Photography (left) and schematic (right) of the DoSi wafer with a diameter of 10 cm.
- (B) SEM image of the edge of DoSi wafer showing boron doped diamond (BDD) film with the resistivity of <0.1 ohm-

cm on the p-type Si <100> (resistivity of 0.01-0.02 ohm-cm).



#### Figure S14. Fabrication procedure of the DoSi wafer electrode for persulfate production.

Step 1, the back side (i.e., bottom silicon side) of the cut DoSi wafer with desired size was cleaned using 24 w% hydrofluoric acid to remove the residual silicon oxide. Step 2-3, the back side of the DoSi wafer was contacted to a piece of Cu foil, which is fixed on a piece of glass, with Gallium-Indiumeutectic (Sigma Aldrich). Step 4-5, epoxy resin (Loctite, EA9460) was used to seal the contact area and cover the edge and back side of the DoSi wafer to expose only the diamond film. The epoxy resin was allowed to cure at room temperature. The copper foil current collector was then folded and inserted into a glass tube, which was also sealed by epoxy to prevent contact with electrolyte during operation.



Figure S15. Electrochemical measurement of the DoSi electrode in 1.7 M Na<sub>2</sub>SO<sub>4</sub> electrolyte.

- (A) CV curves with and without iR correction.
- (B) The corresponding Tafel plot without iR correction of the DoSi electrode measured at a scan rate of 10 mVs<sup>-1</sup> in 1.7

M Na<sub>2</sub>SO<sub>4</sub> electrolyte.

#### Supplemental experimental procedures: detection and determination of the concentration of S2O82-

The concentration of the electrochemically produced  $S_2O_8^{2-}$  was detected with a spectrophotometric method based on iodometric titration.<sup>3</sup> The calibration curves were first constructed by preparing a series of 40 mL standard solutions by mixing DI water, NaHCO<sub>3</sub> (0.2 g), KI (4 g) ( $\geq$  99%, Sigma-Aldrich) and various volume of 0.02 mol/L sodium persulfate stock solution. The resulting solutions (40 mL) were well-mixed by hand shaking and allowed to equilibrate for 15 min. As shown in Figure S16, two corresponding calibration curves for standard Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solutions with the concentration ranges of 0-0.04 mM and 0-0.006 mM were presented, respectively.

For the analysis of produced  $S_2O_8^{2-}$ , 400 µL of the solution withdrawn from the sample solution containing electrochemically generated persulfate was added into this 40 mL NaHCO<sub>3</sub>/KI chromogenic solution for spectrophotometric measurement. Note that the volume changes in the measurement solutions were taken into account for calculating the product concentrations.



Figure S16. The iodometric persulfate method used to determine the concentration of  $S_2O_8^{2-}$ .

 $(A) \ Absorption \ spectra \ of \ iodometric \ solutions \ (KI + NaHCO_3 \ in \ DI \ water) \ containing \ different \ standard \ concentrations \ of \ Na_2S_2O_8 \ solution.$ 

 $(B-C)\ Calibration\ curves\ derived\ from\ the\ UV-V is\ absorbance\ at\ 352\ nm\ for\ standard\ Na_2S_2O_8\ solutions\ with\ concentration\ ranges\ of\ 0-0.04\ mM\ and\ 0-0.006\ mM,\ respectively.$ 

#### Section S3. NaNiHCFRR enabled ModES cycle for H<sub>2</sub>O<sub>2</sub> and S<sub>2</sub>O<sub>8<sup>2-</sup></sub> production

As shown in **Figure S17**, a heterogeneous redox reservoir (RR) electrode was swapped between  $\text{Cell}_{H_2O_2}$  and  $\text{Cell}_{S_2O_8^2}$ . Before placing the RR electrode into the other cell, it was washed using 1.0 M Na<sub>2</sub>SO<sub>4</sub> solution to avoid bringing contaminations of the H<sub>2</sub>O<sub>2</sub> or Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> chemicals into the other cell. Besides the potential of the RR electrode (**Figure S19**) during the ModES cycles, the total capacity (oxidation/ reduction to 100%/ 0% SOR) of the RR electrode is also a key parameter to evaluate its stability during the synthesis of H<sub>2</sub>O<sub>2</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. Therefore, the full capacity of the RR electrode was measured by galvanostatic redox curves after it was used for an arbitrary number of ModES cycles (**Figure S21**). Compared with the initial capacity of 9.2 C, the full capacity of the RR electrode decreased to 8.3 C after 100 ModES cycles of H<sub>2</sub>O<sub>2</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> synthesis, corresponding to a decay rate of 0.09%/ cycle<sub>ModES</sub>.



Figure S17. Step-wise illustration of the NaNiHCF RR enabled ModES in one cycle to separately produce  $H_2O_2$  (step 1) and  $Na_2S_2O_8$  (step 2) in different cells (Cell<sub> $H_2O_2$ </sub> and Cell<sub> $S_2O_8^2$ </sub>).

The corresponding crystal phase transitions of the NaNiHCF RR electrode are also presented.



Figure S18. Potential and voltage profiles during the co-production of H<sub>2</sub>O<sub>2</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in heterogeneous RR enabled ModES system by operating the NaNiHCF-10 RR electrode within a SOR range of 25% to 75%.

(A) Potential of the RR electrode (Potential<sub>RR</sub>) when coupled with the cathodic HPR at  $-0.1 V_{SHE}$  (blue line, oxidation) and anodic PSR at  $2.74 V_{SHE}$  (red line, reduction) over ten continuous cycles.

(B) The corresponding cell voltage (V\_{cell, H\_2O\_2} and V\_{cell, S\_2O\_8^2}) during the ten cycles.



Figure S19. Stability test of the NaNiHCF-10 RR electrode in the ModES system for continuous on-demand production of H<sub>2</sub>O<sub>2</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.

Potential of the RR electrode (Potential<sub>RR</sub>) when coupled with the cathodic HPR at  $-0.1 V_{SHE}$  (blue line, oxidation) and anodic PSR at 2.74  $V_{SHE}$  (red line, reduction) over 100 continuous cycles. The RR electrode showed a very stable potential profile throughout the whole cycling test, indicating the robustness of the heterogeneous RR electrode during the modular production of H<sub>2</sub>O<sub>2</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.



Figure S20. The comparison of the PXRD patterns of the NaNiHCF-10 RR ( $2 \times 2 \text{ cm}^2$  electrode, 36.5 mg mass loading) before and after continuous operation in the ModES system for the production of H<sub>2</sub>O<sub>2</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.

The RR electrode showed no obvious change in the crystal structure after long term operation. The peaks marked with "\*" are attributed to the Ti mesh current collector.



# Figure S21. The full capacity of the NaNiHCF-10 RR electrode ( $2 \times 2 \text{ cm}^2$ electrode, 36.5 mg mass loading) used in the ModES system for the production of H<sub>2</sub>O<sub>2</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.

The decay rate of this RR was around 0.09% per cycle (i.e., 0.26% per hour) in ModES system.



Figure S22. The stability of a NaNiHCF-10 RR electrode (1×1 cm<sup>2</sup>) oxidized and reduced with a long storage period in between.

The RR electrode was first oxidized at 10 mA in 1.7 M Na<sub>2</sub>SO<sub>4</sub>, then rested for 3.5 h outside the solution, followed by being reduced in the same solution at the same current. There is no obvious decay in the capacity between the oxidation and reduction steps, both with a high CE of around 99%. This result suggests that the RR<sup>ox</sup> electrode taken from  $Cell_{H_2O_2}$  can be stored for a desired amount of time before being reduced (to form RR<sup>red</sup>) in  $Cell_{S_2O_8^2}$ -without capacity loss.



Figure S23. The relationship between the total capacity, as well as the corresponding concentration of produced chemicals, and the size and number of the NaNiHCF-10 RR electrode with the same thickness range.

(A) The relationship between the total capacity and the size of the RR electrode with the thickness of  $100-130 \,\mu\text{m}$ , showing the total capacity of the RR electrode increases linearly as the electrode area increases, accompanied with the increased concentration of produced H<sub>2</sub>O<sub>2</sub> and S<sub>2</sub>O<sub>8</sub><sup>2-</sup>.

(B) The total capacity and the corresponding concentrations of produced chemicals within one ModES cycle scale with the number of stacked RR electrodes with the same area and mass loading.



Figure S24. Electrochemical performance of NaNiHCF-10 reservoir in saturated NaCl electrolyte.

Cycling performance at 100 mA/g for 110 cycles and the corresponding Coulombic efficiency of NaNiHCF-10 reservoir from 0.2 V to 1.0 V (vs SHE) in the saturated NaCl electrolyte.

#### Supplemental experimental procedures: active chlorine detection.

To determine the FE for the active chlorine production reaction (ACR, Cl<sup>-</sup>-2e<sup>-</sup> $\rightarrow$ Cl<sub>2</sub>; Cl<sub>2</sub> +H<sub>2</sub>O  $\rightarrow$  HCl + HClO),<sup>4,5</sup> the concentration of the active chlorine in the solution generated by chronoamperometry (CA) was first roughly detected using active chlorine strips (Hach 2745050 Free & Total Chlorine Test Strips, 0-10 mg/L, Inset of **Figure S25**A). The exact concentration was then further measured by the iodometric method.<sup>6</sup> Specifically, the following steps were taken: 1) 5.0 mL of solution was withdrawn from the sample solution containing electrochemically generated active chlorine, 1.000 g KI ( $\geq$  99%, Sigma-Aldrich) was first added and the solution pH was modified to ~3.7 with 10.0 mL acetate buffer solution. The color of the sample solution changed to yellow. 2) Then, the sample solution was titrated using 0.250 mM standard Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> 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 0.250 mM standard Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution until the produced active chlorine in the solution was calculated by recording the volume of the 0.250 mM standard Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution *via* the equation S4-S6.

$$Cl_2 + 2I^- \rightarrow I_2 + 2Cl^-$$
(S4)

$$HClO + 2 I^{-} \rightarrow I_{2} + Cl^{-} + OH^{-}$$
(S5)

$$2 \operatorname{Na}_2 S_2 O_3 + I_2 \twoheadrightarrow \operatorname{Na}_2 S_4 O_6 + 2 \operatorname{NaI}$$
(S6)

All sample solution analysis was conducted by taking 5 mL electrolytes containing active chlorine produced after CA processes. The FE for ACR is calculated using the following equation S7.

FE (%)= 
$$\frac{Q \text{ for AC production}}{Q_{input}} \times 100 = \frac{[AC] \times V \times 2 \times 96485}{Q_{input}} \times 100$$
 (S7)

where V, [AC] and Q<sub>input</sub> are the volume of the electrolyte, concentration of produced active chlorine and the input charge during the CA electrolysis processes, respectively.



Figure S25. Electrochemical active chlorine (AC) production in individual cells with separator.

(A) CV curve (without *iR* compensation) measured at a scan rate of  $10 \text{ mV s}^{-1}$  and the corresponding potential-dependent Faradaic efficiency of dimensionally stable anode (DSA) for producing active chlorine in saturated NaCl electrolyte. Inset, the active chlorine test strip detection of the produced active chlorine in saturated NaCl electrolyte.

(B) The chronoamperometry curves of DSA electrode at various potentials (V versus SHE) in saturated NaCl electrolyte with 4 C of input charge.



Figure S26. Step-wise illustration of the NaNiHCFRR enabled ModES process in one cycle to separately produce  $H_2O_2$  (step 1 in Na<sub>2</sub>SO<sub>4</sub> electrolyte) and active chlorine (AC) (step 2 in NaCl electrolyte) in different cells (Cell<sub>H<sub>2</sub>O<sub>2</sub> and Cell<sub>AC</sub>).</sub>



Figure S27. Voltage profiles and the corresponding VE during the co-production of H<sub>2</sub>O<sub>2</sub> and AC in heterogeneous RR enabled ModES system by operating the NaNiHCF-10 RR electrode within a SOR range of 25% to 75%.

(A) The cell voltage (V\_{cell,\,H\_2O\_2} and ~V\_{cell,\,AC}) profiles during the 10 ModES cycles.

(B) The corresponding average cell voltages  $(V_{cell})$  of  $Cell_{H_2O_2}$  and  $Cell_{AC}$  in 10 representative cycles. The error bars shown are the range of the potential profiles of the whole cell. **c**. The corresponding VE of this ModES process for H<sub>2</sub>O<sub>2</sub> and AC production.

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