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Abstract

Electrochemical hydrogen peroxide (H_2O_2) synthesis via two-electron oxygen reduction reaction (2e^- ORR) offers a sustainable alternative to the anthraquinone process, yet practical deployment remains limited by insufficient selectivity, low system-level value, and reliance on freshwater electrolytes. Here we report a photovoltaic-driven single-atom electrocatalyst cell (PV-SAEC) that enables bias-free co-production of H_2O_2 production with chlorine (Cl_2) directly from saline feedstocks. A bio-inspired Ni single-atom catalyst, mimicking the second coordination environment of nickel superoxide dismutase, promotes efficient alkaline 2e^- ORR, while a Pt single-atom catalyst selectively catalyzes chlorine evolution at the anode. Under one-sun illumination and zero applied bias, the integrated PV-SAEC system simultaneously produces H_2O_2 and Cl_2 , while desalinating seawater. Techno-economic and life-cycle analyses reveal clear economic and environmental advantages over incumbent anthraquinone and chlor-alkali processes, establishing a scalable platform for multifunctional seawater valorization.

Introduction

Hydrogen peroxide (H_2O_2) is an indispensable commodity chemical that underpins industries spanning from chemical synthesis and pulp and paper bleaching to semiconductor processing and wastewater treatment^{1,2}. Owing to its versatility as an oxidizing agent and environmentally benign nature, global demand for H_2O_2 continues to increase across both industrial and environmental sectors. As an alternative to the traditional anthraquinone process, electrochemical H_2O_2 synthesis via the two-electron oxygen reduction reaction (2e^- ORR) enables a sustainable route to decentralized, on-site, and continuous generation of H_2O_2 under mild operating conditions using only O_2 and H_2O ^{3–5}. However, ORR proceeds through catalyst-dependent competing pathways. Selective H_2O_2 formation requires optimal binding energy of

*OOH intermediate; otherwise, the thermodynamically favored H₂O-producing four-electron ORR dominates. Furthermore, the produced H₂O₂ is susceptible to further electrochemical reduction. Accordingly, the development of electrocatalysts that selectively steer ORR toward H₂O₂ remains challenging.

From a system-level perspective, many reported electrochemical H₂O₂ production platforms mostly pair cathodic 2e⁻ ORR with anodic O₂ evolution reaction (OER), resulting in co-production of H₂O₂ and O₂ (refs. 4, 6, 7). While electrochemically convenient, O₂ is a relatively low-value product with a mature supply chain, providing limited economic incentive. Moreover, these systems typically rely on purified freshwater electrolytes, which increases operational cost and constraints scalability.

To address these challenges, we propose a photovoltaic-driven single-atom electrocatalyst cell (PV-SAEC) platform that employs saline as the electrolyte and replaces anodic OER with the chlorine evolution reaction (CER)^{8,9} (**Fig. 1**). This design enables the simultaneous generation of two value-added chemicals, H₂O₂ at the cathode and Cl₂ at the anode, while providing concurrent desalination. By integrating selective H₂O₂ electrosynthesis with CER in a single device, this platform transforms seawater into multiple valuable outputs, offering a fundamentally different and systemically advantageous alternative to conventional H₂O₂/O₂ systems.

Realizing such an integrated H₂O₂/Cl₂ co-production system requires highly active and selective catalysts for both half-reactions. Here we present a unified single-atom catalyst (SAC) materials platform that enables efficient production of both H₂O₂ and Cl₂. As the cathodic catalyst, we design a Ni-based SAC inspired by the metalloenzyme nickel superoxide dismutase (Ni SOD), which selectively catalyzes the disproportionation of O₂^{•-} into H₂O₂ and O₂ (refs. 10, 11). Ni SOD features a square-planar Ni²⁺-N₂S₂ first coordination shell, surrounded by a second coordination environment comprising a phenolic group of tyrosine (Tyr9) and amine

functionalities of cysteine residues (Cys2 and Cys6). Guided by this structural motif, we synthesize a Ni SAC that emulates the Ni SOD-like second coordination environment (**Fig. 2a**). By preserving the Ni first coordination shell while systematically reconstructing surface functionalities, we find that edge phenolic and amine groups synergistically interact with a distorted square planar $\text{Ni}^{2+}\text{-N}_4$ active sites to enhance alkaline 2e^- ORR activity. For Cl_2 production, we employ a Pt-based SAC¹², recently developed by Joo *et al.*, as a highly active and selective catalyst.

With Ni- and Pt-based SACs as the cathode and anode catalysts, respectively, the PV-SAEC system operates under one-sun illumination without external bias, co-producing H_2O_2 and Cl_2 with faradaic efficiencies (FEs) of 83 and 79%, respectively, using only O_2 and aqueous NaCl. Notably, Na^+ and Cl^- ions are simultaneously electrodialed during operation, imparting an additional desalination function. Stable operation with comparable selectivity is demonstrated in real seawater, highlighting the robustness and feedstock flexibility of the system. The evaluation of practical feasibility of the PV-SAEC system through techno-economic analysis (TEA) and life cycle assessment (LCA) based on an industrial-scale plant model reveals that the PV-SAEC system offers clear economic and environmental advantages over incumbent anthraquinone and chlor-alkali processes.

Results

Preparation and characterization of Ni SACs

To emulate the second coordination environment of the Ni SOD cofactor (**Fig. 2a**), we designed a series of Ni single-atom catalysts (denoted *X*-Ni SACs) in which the overall structure and Ni first coordination shell are preserved, while the surrounding surface functionalities are systematically modulated. The synthesis of *X*-Ni SACs (**Supplementary Fig. 1**) began with infiltration of nickel acetate and 1,10-phenanthroline into the mesopores of hexagonally ordered

mesoporous silica SBA-15. Subsequent pyrolysis and removal of the silica template and residual Ni particles yielded the as-prepared catalyst (RT-Ni SAC), which contains diverse surface functionalities including phenolic and amine groups (see Methods). To induce surface diffusion and rearrangement of heteroatom species initially binding to metastable carbon sites and to drive their migration toward thermodynamically favored and structurally flexible carbon edge sites^{13–16}, RT-Ni SAC was subjected to post-heat treatments at 300, 600, and 700 °C, affording the LT-, IT-, and HT-Ni SACs, respectively.

We first confirm that structural properties and Ni first coordination environment remain essentially invariant across the four *X*-Ni SACs. Small-angle X-ray diffraction (XRD) patterns (**Supplementary Fig. 2**) reveal the formation of hexagonal mesostructured for all catalysts, indicating faithful replication of the SBA-15 template. All catalysts exhibit similar N₂ adsorption–desorption isotherms, and the corresponding Barrett-Joyner-Halenda (BJH) pore size distribution curves show mesopores at 4.5–5 nm and 30 nm, arising from removal of the silica template and large Ni particles, respectively (**Supplementary Fig. 3**). The *X*-Ni SACs catalysts possess comparable Brunauer–Emmett–Teller (BET) surface areas (715–747 m² g^{−1}) and total pore volumes (1.46–1.57 cm³ g^{−1}) (**Supplementary Table 1**). Inductively coupled plasma optical emission spectroscopy (ICP-OES) and combustion analysis (**Supplementary Table 2**) indicate similar amounts of Ni and N species across the series, whereas H and O contents decrease with increasing post-heat-treatment temperature.

We next scrutinize the nature of Ni species in *X*-Ni SACs. Wide-angle XRD patterns (**Supplementary Fig. 2**) show only amorphous and graphitic carbon features around 22° and 26°, respectively, with no detectable crystalline Ni phases, suggesting atomic dispersion of Ni within the carbon matrix. The Ni species in *X*-Ni SACs is further identified by transmission electron microscopy (TEM). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy images

(**Supplementary Fig. 4**) reveal uniform distribution of Ni, C, N, and O throughout the catalysts. High-magnification HAADF-STEM images (**Fig. 2b** and **Supplementary Fig. 5**) show isolated bright spots corresponding to single Ni sites. Deconvolution of the N 1s X-ray photoelectron spectroscopy (XPS) spectra (**Supplementary Fig. 6a**) identifies Ni–N_x species, along with pyridinic N, pyrrolic N, graphitic N, and N⁺–O[–] species, corroborating the microscopy results.

The single-atomic nature of *X*-Ni SACs is further verified with extended X-ray absorption fine structure (EXAFS) spectra (**Fig. 2c**), which display a single dominant peak at 1.27 Å corresponding to the Ni–N coordination, with no evidence for Ni–Ni scattering. EXAFS fittings based on a Ni–pyridinic N coordination model incorporating the off-centered geometry (**Supplementary Figs. 7 and 8** and **Supplementary Table 3**) yields coordination numbers of 3.9–4.0 and Ni–N bond lengths of 1.85–1.87 Å for all catalysts. Ni K-edge X-ray absorption near-edge spectroscopy (XANES) spectra of all *X*-Ni SACs (**Fig. 2d**) are nearly identical across the series, confirming preservation of the first coordination environments. Compared with Ni phthalocyanine (NiPc), which exhibits a pronounced pre-edge peak B characteristic of an ideal square-planar Ni–N₄ geometry, *X*-Ni SACs show a markedly attenuated peak B accompanied by a slightly enhanced peak A, indicating partial symmetry breaking around the Ni centers. Subtle changes in the post-edge region, where a progressive decrease in peak D relative to peak C with increasing treatment temperature, further support the presence of an off-centered square-planar Ni–N_x structure^{17,18}. Consistently, Ni 2p XPS spectra of *X*-Ni SACs (**Supplementary Fig. 6b**) display characteristic doublets around 855 and 872 eV with satellite features, indicating a near Ni²⁺ oxidation state.

Having established invariant first coordination environment, we next examine the second coordination environment of *X*-Ni SACs. Near edge X-ray absorption fine structure (NEXAFS), Fourier-transform infrared spectroscopy (FT-IR), and cyclic voltammetry (CV) were employed

to identify specific surface functionalities^{18–23}. C K-edge NEXAFS spectra (**Supplementary Fig. 9**) show an increase in the $\pi^*(\text{C}=\text{C}$ and $\text{C}=\text{N})$ feature near 284 eV and a decrease around 288 eV with increasing heat-treatment temperature, indicating enhanced aromaticity accompanied by the loss of heteroatom-containing functionalities. Because of spectral overlap, unambiguous assignment of individual surface functionalities from the C K-edge spectra alone is challenging¹⁹; this limitation is resolved by O and N K-edge NEXAFS analyses. O K-edge NEXAFS spectra (**Fig. 2e**) reveal a gradual attenuation of the carbonyl $\pi^*(\text{C}=\text{O})$ feature at 533 eV from RT- to HT-Ni SAC, consistent with the diminishing carbonyl redox signals observed in the CV measurements (**Supplementary Fig. 10**)^{18,19}. Notably, the phenolic $\pi^*(\text{C}-\text{O}, \text{O}-\text{H})$ feature exhibits a pronounced shift to higher energy for IT-, and HT-Ni SACs, indicating preferential formation of phenolic groups at carbon edge following heat treatment at 600 °C^{13,15,16,19}. Similarly, N K-edge NEXAFS spectra (**Fig. 2f**) show a higher energy shift of the amine $\sigma^*(\text{C}-\text{N})$ feature exclusively in HT-Ni SAC, suggesting that the formation of edge-localized amine groups is promoted at 700 °C^{14,16,20,21}.

FT-IR spectroscopy (**Fig. 2g**) further substantiates the formation of heteroatom functionalities^{19,22,23}. All *X*-Ni SACs catalysts exhibit characteristic vibrational modes associated with Ni–N (525 cm^{-1}), aromatic C=C (1575 cm^{-1}), O- and N-containing functionalities (1,000–1,350, 1,645, and 3,500 cm^{-1}). RT-Ni SAC additionally exhibits broad molecular-type vibrational modes, including C–H stretching (2,700–3,050 cm^{-1}), O–C=O stretching (1,730 cm^{-1}), C–N stretching (1,025 cm^{-1}), and out-of-plane C–H bending (675–780 cm^{-1}). These features largely disappear after 300 °C treatment (LT-Ni SAC), indicating removal of weakly bound surface species. At higher temperatures, new low-frequency bands emerge: IT-Ni SAC displays an out-of-plane O–H wagging (530–650 cm^{-1}) characteristic of edge phenolic groups²², which persists in HT-Ni SAC together with an additional band at 570 cm^{-1} attributable to out-of-plane N–H wagging, signaling formation of edge amine groups²³.

Collectively, these results demonstrate a temperature-dependent and systematic evolution of surface functionalities in *X*-Ni SACs. Low-temperature (300 °C) annealing primarily removes weakly bound molecular species, whereas higher-temperature treatments selectively stabilize phenolic (600 °C) and amine (700 °C) groups at carbon edge sites without perturbing the off-centered Ni²⁺-N₄ first coordination shell. This strategy yields a set of model catalysts that progressively emulate the second coordination environment of the Ni-SOD cofactor, culminating in IT- and HT-Ni SACs, which partially and most closely reproduce the enzyme-inspired second-sphere architecture, respectively (**Fig. 2a**).

Electrochemical 2e⁻ ORR performance *X*-Ni SACs

The electrocatalytic activity and selectivity of *X*-Ni SACs toward 2e⁻ ORR were investigated under alkaline conditions (0.1 M KOH) using the rotating ring-disk electrode (RRDE) method. Electrochemical impedance spectroscopy (EIS) measured at 0.6 V (vs. reversible hydrogen electrode, RHE) (**Supplementary Fig. 11**) reveals comparable solution resistances for all catalysts, indicating similar bulk solution conductivity²⁴. In addition, all catalysts exhibit strongly suppressed H₂O₂ reduction (HPR) currents (**Supplementary Fig. 12**), confirming their intrinsic preference for selective H₂O₂ production²⁵.

Linear sweep voltammetry (LSV) curves (**Fig. 3a**) show an increasing activity trend of LT- < RT- < IT- < HT-Ni SAC, which aligns with the trend in charge transfer resistance extracted at 0.6 V (vs. RHE) (**Supplementary Fig. 11**). All catalysts exhibit comparable H₂O₂ selectivity (**Fig. 3b**), indicating that activity differences predominantly reflect intrinsic 2e⁻ ORR activity. LT-Ni SAC shows the lowest activity and selectivity, which can be attributed to the partial removal of ORR-promoting heteroatom functionalities, particularly carbonyl species, during 300 °C treatment (**Figs. 2g and 3b and Supplementary Fig. 10**). Compared with RT-Ni SAC, IT-Ni SAC exhibits 10 mV lower overpotential due to synergistic interaction between edge

phenolic groups and the off-centered square-planar $\text{Ni}^{2+}\text{-N}_4$ site. HT-Ni SAC shows a further 28 mV overpotential decrease enabled by additional cooperation with edge amine groups.

X-Ni SACs exhibit similar Tafel slopes within a narrow range (46.4–57.3 mV dec⁻¹) (**Fig. 3c**), suggesting a common rate-determining step. The narrow distribution indicates that the observed activity differences arise from modulation of the second coordination environment rather than changes in the fundamental reaction mechanism²⁶. In bulk electrolysis (**Fig. 3d**), the best-performing HT-Ni SAC sustains a stable current (6.2 mA) for 24 h, delivering 89.2% H₂O₂ FE and an accumulated H₂O₂ concentration of 61.7 mM. Benchmarking against previous reported SACs and carbon-based catalysts makes HT-Ni SAC one of the best H₂O₂-producing electrocatalysts with the highest mass activity at 0.8 V (vs. RHE) and favorable H₂O₂ selectivity (**Fig. 3e and Supplementary Table 4**)^{19,26–45}.

Turnover frequency (TOF) calculation of Ni SACs

To quantify the intrinsic activity of *X*-Ni SACs, TOFs were calculated by normalizing current to the number of active sites. Potassium thiocyanate (KSCN) poisoning experiments (**Supplementary Fig. 13**) reveal a pronounced and reproducible decrease in ORR activity for all *X*-Ni SACs, confirming that the off-centered square-planar $\text{Ni}^{2+}\text{-N}_4$ moiety serves as the dominant active site. Site densities (*SDs*) were quantified via in situ cyanide (CN^-) titration (**Figs. 4a,b and Supplementary Fig. 14**) by correlating CN^- uptake with the corresponding decrease in ORR current⁴⁶. Assuming that the observed current loss arises from poisoning of $\text{Ni}^{2+}\text{-N}_4$ sites (**Fig. 4c and Supplementary Fig. 13**), the extracted Ni TOFs follow HT- > IT- > RT- > LT-Ni SAC across the examined potential range (**Supplementary Fig. 15**). Notably, at 0.8 V (vs. RHE), the IT-Ni SAC exhibits a 2.1-fold higher Ni TOF than RT-Ni SAC, while HT-Ni SAC achieves a more pronounced 7.5-fold enhancement (**Fig. 4d**), highlighting the role of synergistic interaction between edge phenolic and amine groups and off-centered square

planar $\text{Ni}^{2+}\text{-N}_4$ sites in boosting the intrinsic activity of Ni sites in *X*-Ni SACs.

Construction of PV-SAEC system for co-production of H_2O_2 and Cl_2 with desalination

We next construct a PV-SAEC system that enables the simultaneous co-production of H_2O_2 and Cl_2 with electrodialysis-based desalination. The reactor integrates two electrodes and three physically separated electrolyte compartments (**Figs. 1 and 5a and Supplementary Fig. 16**). The newly synthesized HT-Ni SAC was used as the cathodic 2e^- ORR and Pt SAC developed in our group¹² served as the anodic CER catalyst. The single-atomic dispersion of Pt species in Pt SAC is confirmed by wide-angle XRD and HAADF-STEM analyses (**Supplementary Fig. 17**), and its high activity and selectivity for CER is also verified (**Supplementary Fig. 18**). A three-cell silicon PV module supplies power to the system. We note that the ORR on HT-Ni SAC is intrinsically limited by oxygen mass transport due to reliance on dissolved oxygen. This limitation is effectively alleviated by implementing HT-Ni SAC in gas-diffusion electrode (GDE) configuration, which substantially enhances oxygen availability.

Following individual catalyst optimization, the overall PV-SAEC system configuration was refined to accommodate the distinct requirements of the two half-reactions. HT-Ni SAC exhibits optimal H_2O_2 production under alkaline conditions, whereas the Pt SAC shows maximal CER activity in chloride-containing acidic media. Accordingly, 1.0 M NaOH was used as the catholyte for the HT-Ni SAC/GDE, while 0.1 M HClO_4 + 1.0 M NaCl served as the anolyte for the Pt SAC/hydrophobic carbon paper (CP) (**Supplementary Fig. 19**). A 1.0 M NaCl solution was employed in the desalination compartment to match the chloride concentration of the anolyte and ensure stable ion transport. To prevent electrolyte cross-contamination, the system employed fully separated compartments using two membranes. A sodium superionic conductor (NASICON) membrane and an anion exchange membrane (AEM) were placed between the ORR–desalination and CER–desalination compartments, respectively,

enabling selective Na^+ transport to the ORR side and Cl^- migration to the CER side.

The two-electrode polarization curve of the SAEC (**Fig. 5b**) indicates that the overall electrochemical reaction initiates at 1.25 V. Upon direct coupling with the PV module, the PV-SAEC operating point is established at 1.68 V and 10.1 mA, enabling fully bias-free operation with simultaneous generation of H_2O_2 and Cl_2 . Notably, this operating point (17.0 mW at 1.68 V) is close to the maximum power point (P_{Max}) of the PV module (17.4 mW at 1.59 V), demonstrating efficient electrical matching and near-optimal solar energy utilization (**Supplementary Fig. 20**)⁴⁷.

Product accumulation was evaluated in a closed system using three consecutive 1 h electrolysis cycles (**Fig. 5c**). Under these conditions, the PV-SAEC system produces H_2O_2 and Cl_2 simultaneously with high FEs of 83 and 79 %, respectively (**Fig. 5d**). To mitigate catalyst deactivation associated with Cl_2 ⁴⁸ and to assess long-term stability, the system is subsequently operated in a flow-cell configuration (**Fig. 5e**). The PV-SAEC system sustains a stable current of 9.89 mA for 30 h, demonstrating durable co-production of H_2O_2 and Cl_2 . Ion chromatography analysis reveals reductions of 21% in Na^+ and 7% Cl^- concentrations in the desalination compartment (**Fig. 5f**). The asymmetric ion removal is attributed concurrent OH^- transport through the AEM, leading to pH reduction from 6.3 to 3.3 in closed system and to 3.2 under flow conditions (**Supplementary Fig. 21**).

Finally, the robustness and applicability of the PV-SAEC system were demonstrated using seawater (**Supplementary Figs. 22 and 23**). Although lower operating currents are observed due to the reduced Na^+ and Cl^- concentrations, the system maintains high FEs of 79% for H_2O_2 and 80% for Cl_2 . Importantly, the desalination compartment pH decreases from 7.9 to 6.1, which lies within the typical range of conventionally desalinated seawater (5.0–6.5), suggesting the practical relevance and scalability of the PV-SAEC platform.

Techno-economic analysis (TEA) and life-cycle assessment (LCA) of PV-SAEC

To quantitatively benchmark the economic and environmental potential of the PV-SAEC system against established commercial routes (anthraquinone and chlor-alkali processes), comprehensive TEA and LCA were conducted. Both analyses are based on the industrial-scale plant models with a daily production capacity of 100,000 kg H₂O₂, using material and energy balances derived from experimentally measured electrochemical parameters. The TEA–LCA boundary is defined around an H₂O₂ scenario (**Supplementary Fig. 24**), in which PV electricity drives an electrochemical cell converting NaCl, H₂O, and O₂ into an alkaline H₂O₂ stream and Cl₂-rich gas stream. Unreacted O₂ is recycled, Cl₂ is purified via gas–liquid separation, and alkaline H₂O₂ effluent is directly collected as the basis for sales. Consumption of NaCl concurrently lowers brine salinity, providing an intrinsic desalination co-benefit (**Supplementary Note 1**).

FE emerges as the dominant performance metric governing economic viability (**Fig. 6a**). When the alkaline H₂O₂ stream is sold directly, an FE of 70% already yields a levelized minimum selling price (LMSP) of 1.01 US\$ per kg H₂O₂, within the current market range (1.0–1.2 US\$ per kg H₂O₂). At the experimentally achieved FE of 84.3% (base case), the LMSP decreases to 0.71 US\$ per kg H₂O₂ and could be further reduced to 0.48 US\$ per kg H₂O₂ at 100% FE. Accounting for the desalination co-benefit provides an additional annual cost saving of 1.39×10⁵ US\$ in the base case. Further value creation could be achieved through downstream utilization of alkaline H₂O₂ in chemical synthesis, such as propylene oxide production (**Supplementary Fig. 24, Supplementary Tables 5 and 6, and Supplementary Note 1**)⁴⁹.

Cost breakdown analysis reveals that the PV-SAEC system is strongly capital expenditure (CAPEX)-dominated (**Fig. 6b and Supplementary Table 7**). Approximately 80% of the levelized H₂O₂ cost is attributed to CAPEX, primarily associated with the electrochemical stack (catalysts and membranes) and installation, followed by balance-of-plant components.

Operating expenditure (OPEX) contributes to the remaining 20%, dominated by chemical feedstock costs, while utilities and operation and maintenance costs account for a minor fraction. This cost structure reflects the replacement of grid electricity and steam with PV power, suggesting that future cost reduction will primarily arise from lowering stack and installation costs.

The specific energy consumption (SEC) of PV-SAEC process is 34.3 GJ per ton H_2O_2 and 16.6 GJ per ton Cl_2 , substantially lower than that of the anthraquinone (67 GJ per ton H_2O_2) and chlor-alkali (47.8 GJ per ton Cl_2) processes (**Figs. 6c,f**). Because the electrochemical unit is powered by solar energy, only 22.3 GJ per ton H_2O_2 and 10.8 GJ per ton Cl_2 are required, underscoring the reduced grid dependency of the PV-SAEC system. LCA further highlights the environmental advantages of the PV-SAEC system. The global warming potential (GWP) reaches -0.17 kg CO_2 -eq per kg H_2O_2 and -0.06 kg CO_2 -eq per kg Cl_2 , in stark contrast to 2.16 kg CO_2 -eq per kg H_2O_2 and 1.06 kg CO_2 -eq per kg Cl_2 for the anthraquinone and chlor-alkali processes, respectively (**Figs. 6d,g**). These net-negative emissions arise from displacement credits and the replacement of fossil-derived energy with solar power. Beyond GWP, the PV-SAEC system shows consistent reductions across multiple midpoint indicators, including acidification potential, freshwater ecotoxicity potential, human toxicity potential, marine ecotoxicity potential, and abiotic depletion potential for fossil fuels, confirming its potential as a climate-positive and environmentally superior manufacturing route for H_2O_2 and Cl_2 (**Figs. 6e, h and Supplementary Tables 8 and 9**).

Discussion

In summary, we have demonstrated a photovoltaic-driven single-atom electrocatalyst cell that enables the integrated co-production of hydrogen peroxide and chlorine directly from saline and seawater. Inspired by the second coordination environment of nickel superoxide dismutase,

we design a highly active and selective H₂O₂-producing Ni-based SAC in which edge-localized phenolic and amine groups synergistically enhance the intrinsic activity of square-planar Ni²⁺–N₄ single-atom sites. At the system level, pairing the optimized HT-Ni SAC-based cathode with a Pt SAC-based anode for chlorine evolution creates a fundamentally different electrochemical architecture from conventional H₂O₂/O₂ platforms. The resulting PV-SAEC achieves solar-driven, bias-free co-production of two value-added chemicals while simultaneously desalinating seawater. Stable operation in real seawater, together with favorable techno-economic and life-cycle assessments, highlights the scalability and sustainability of this approach relative to incumbent anthraquinone and chlor–alkali processes.

Methods

Chemicals

Pluronic P123 ($M_n = 5800$), tetraethyl orthosilicate (98%), 1,10-phenanthroline (99%), K₃[Fe(CN)₆] (99%), KCN (99%), KSCN (99%), H₂SO₄ (99.999%), KI (>99.5%), (NH₄)₆Mo₇O₂₄ • 4H₂O (>99%), NH₄NO₃ (>99%), KOH (99.99%), NaOH (99.99%), methanol (>99.8%), Nafion solution (5 wt%), *N, N*-diethyl-*p*-phenylenediamine sulfate (DPD, >80.0%), peroxidase (POD), Na₂S₂O₃ (99%), Na₂HPO₄ (>99.0%), NaH₂PO₄ (>98.0%), and HClO₄ (70%) were purchased from Sigma-Aldrich. NaCl, NaOH, HCl (35–37%), HNO₃ (60%), ethanol (94.5%, EtOH), anhydrous EtOH (99.9%), and HF (49%) were purchased from Samchun Chemicals. KNO₃ (99%), standard 0.01 N Na₂S₂O₃ solution, starch, and hydrous nickel acetate (Ni(CH₃COO)₂ • 4H₂O, 99%) were purchased from Alfa Aesar. KBr (for IR spectroscopy Uvasol[®]) was purchased from Supelco. TGP-H-60 carbon paper and starch solution (1% w/v) were purchased from Thermo Scientific. Nafion ionomer (D521, 5 wt% in isopropanol/H₂O) was purchased from Dupont. *p*-Nitrobenzaldehyde solution was purchased from TCI. Si solar cell (KXOB25-04X3F) was purchased from ANYSOLAR. NASICON was purchased from

4science. Anion exchange membrane (AXP-D) was purchased from Astom. HCP020 carbon paper was purchased from Wizmac. All chemicals, membranes, and solar cell were used as received. Deionized (DI) water was obtained using a Millipore Milli-Q system (18.2 M Ω). Seawater was collected from Ilsan beach, Ulsan, Republic of Korea (35°29'49.2''N 129°25'51.6''E). Ar (99.999%), N₂ (99.999%), H₂ (99.999%), and O₂ (99.999%) gases were purchased from KOSEM and SINJIN.

Preparation of Ni SACs and Pt SAC

RT-Ni SAC was synthesized using a nanocasting method. Briefly, 1.0 g of mesoporous silica SBA-15 (**Supplementary Fig. 25**) and 1.0 g of a physical mixture of hydrous nickel acetate and 1,10-phenanthroline (molar ratio 1:3) were ground for 5 min with an agate mortar and pestle. Subsequently, 1.2 mL of DI water was added, and the mixture was further homogenized for 15 min and dried at 60 °C for 6 h. The dried composite was subjected to heat treatment under N₂ flow (1 L min⁻¹) by raising the temperature to 800 °C at a ramping rate of 2 °C min⁻¹ and held at 800 °C for 3 h. After cooling, the product was treated twice with a mixed solution of 4 M HF, 2 M HCl, and EtOH under stirring for 30 min to remove the SBA-15 template and Ni particles. The solid was then filtered, washed with DI water and EtOH until the pH of the filtrate reached 7, and dried overnight at 60 °C to yield RT-Ni SAC. LT-, IT-, and HT-Ni SACs were obtained by post-heat treatment of RT-Ni SAC at 300, 600, and 700 °C, respectively. For each catalyst, RT-Ni SAC was heated to the target temperature at 2 °C min⁻¹ and held for 1 h under N₂ flow (1 L min⁻¹). Pt SAC was synthesized following the previously reported procedure by Joo *et al*¹².

Characterization methods

XRD patterns were collected using a high-power X-ray diffractometer (D/Max 2500V/PC, Rigaku) equipped with a Cu K α radiation source operated at 40 kV and 200 mA. Atomic-scale

HAADF-STEM and EDS mapping images were taken using a Spectra 300 microscope (ThermoFisher Scientific) and a JEM 2100F microscope (JEOL), both operated at 200 kV. The N₂ physisorption measurements were performed using a BELSORP-Max system (MicrotracBEL). Prior to analysis, samples were degassed under vacuum (10⁻² Pa) at 150 °C for 12 h. Specific surface areas and pore size distributions were determined using the BET method and BJH model, respectively. Ni contents of the X-Ni SAC catalysts were quantified by an ICP-OES analyzer (700-ES, Varian). Prior to ICP-OES analysis, the catalysts were fully digested in aqua regia using a microwave digestion system (Mars 6, CEM) at 220 °C for 30 min (ramping rate of 6.5 °C min⁻¹) and power of 600 W. Elemental compositions (C, H, N, and O) were determined using an elemental analyzer (Flash 2000, Thermo Fisher Scientific) based on the dynamic flash combustion method. The Ni K-edge XAS measurements were conducted at RT at the 6D, 8C, and 10C beamlines of the Pohang Accelerator Laboratory (PAL) in transmittance mode. All spectra were energy calibrated using a Ni foil reference. Catalyst powders were pelletized to an appropriate thickness to ensure suitable X-ray transmittance. Background subtraction and normalization of the XAS data were performed using the Athena software with an R_{bkg} of 1.1 and a Hanning-type window, while EXAFS fitting was carried out using the Artemis software. The passive electron reduction factor (S_0^2) was determined by fitting the EXAFS spectrum of a Ni foil (**Supplementary Fig. 26**). NEXAFS spectra at the C and O K-edges were recorded at the 4D Beamline of the PAL, while the N K-edge spectrum was collected at the 10A Beamline. FT-IR spectra were obtained in transmission mode using an FT-IR spectrometer (Thermo Fisher Scientific). For FT-IR measurements, each sample powder was thoroughly mixed with KBr using a SHAKIR sample grinder (PIKE Technologies) and pressed into pellets. XPS measurements were performed on an ESCALAB 250XI Spectrometer (Thermo Fisher Scientific) using a monochromated Al K α X-ray source. Spectral deconvolution was carried out using XPSpeak41 software with a Shirley-type background and

mixed Gaussian-Lorentzian functions (70:30) line shape.

Electrochemical measurements

All electrochemical experiments were performed at RT using a rotator (AFMSRCE, Pine Research Instrumentation) and bipotentiostat (CHI760E, CH Instruments). A conventional three-electrode configuration was employed, consisting of a catalyst-coated RRDE (AFE7R9GCPT, Pine Research Instrumentation), an Hg/HgO electrode (CHI152, CH Instruments; 1 M KOH filling solution), and a graphite rod as the working electrode, reference, and counter electrodes, respectively. The Hg/HgO reference electrode was calibrated against the RHE prior to use. RHE calibration was conducted in an H₂-saturated 0.1 M KOH electrolyte using a Pt mesh working electrode, where the stable open-circuit potential obtained after 30 min is taken as the RHE conversion value. Prior to catalyst deposition, the RRDE was polished using a microcloth with an aqueous alumina suspension (Allied High Tech Products Inc.) and subsequently ultrasonicated in DI water. Catalyst inks were prepared by dispersing an appropriate amount of the catalyst in a mixture of DI water, Nafion[®], and anhydrous EtOH followed by ultrasonication for 30 min. The ink was drop-cast onto the glassy carbon (GC) disk of the RRDE and dried at 60 °C for 2 min, yielding a catalyst loading of 50 $\mu\text{g cm}^{-2}$. Before each ORR measurement, the catalyst-coated disk was electrochemically cleaned in an N₂-saturated electrolyte by potential cycling between 0.05 and 1.20 V (vs. RHE) for 20 cycles at a scan rate of 100 mV s⁻¹, followed by three CV cycles at 20 mV s⁻¹ in the same potential window. The Pt ring electrode was separately cleaned by cycling between 0.05 to 1.20 V (vs. RHE) for 50 cycles at a scan rate of 500 mV s⁻¹. EIS was conducted at 0.6 V (vs. RHE) over a frequency range from 100 kHz to 0.1 Hz to compensate for the ohmic losses and evaluate the charge transfer resistance. ORR polarization curves were obtained by LSV from 1.1 to 0.4 V at a scan rate of 5 mV s⁻¹ in an O₂-saturated 0.1 M KOH at an electrode rotation speed of 1600 rpm,

while the Pt ring potential was held at 1.3 V. Non-faradaic current (i_{nF}) were corrected by subtracting LSV curves collected under identical conditions in N₂-saturated electrolyte.

After ORR measurements, the RRDE was thoroughly rinsed with DI water and 0.5 M KNO₃ and subsequently immersed in N₂-saturated 0.5 M KNO₃ containing 2 mM K₃[Fe(CN)₆] to determine the collection efficiency (N). CA measurement was performed at −0.2 V (vs. Ag/AgCl) with the ring potential fixed at 0.5 V (vs. Ag/AgCl) for 300 s. The background ring current was measured under identical conditions with the disk potential set to 0.5 V (vs. Ag/AgCl). The N value was calculated according to equation (1):

$$N = \frac{|i_r - i_{r,bg}|}{i_d} \quad (1)$$

where i_r , i_d , and $i_{r,bg}$ represent the ring current, disk current, and background ring current, respectively. Using the experimentally determined N value (**Supplementary Fig. 27**), the H₂O₂ selectivity ($X_{\text{H}_2\text{O}_2}$) was calculated from the ORR polarization curve data using equation (2):

$$X_{\text{H}_2\text{O}_2}(\%) = \frac{200}{1 + \left| \frac{(i_d - i_{\text{nF}})}{i_r/N} \right|} \quad (2)$$

where i_{nF} denotes the non-faradaic background disk current. The kinetic ring current ($i_{k,r}$) value was derived using the Koutecký–Levich relationship (equation (3)):

$$\frac{1}{i_r} = \frac{1}{i_{l,r}} + \frac{1}{i_{k,r}} \quad (3)$$

where $i_{l,r}$ and $i_{k,r}$ are the diffusion-limited current and kinetic current for H₂O₂ production, obtained as the maximum value of i_r/N over the investigated potential range (0.4–1.1 V).

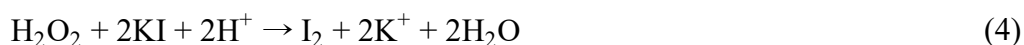
HPR experiments were carried out using LSV measurements from 1.0 to 0.4 V at a scan rate of 5 mV s^{−1} and a rotation speed of 1600 rpm. Background currents were first recorded in N₂-saturated 0.1 M KOH, followed by measurements after the addition of 10 mM of H₂O₂ to the electrolyte.

All electrochemical measurements are independently repeated at least three times, and reported values represent the averaged results.

Bulk electrolysis measurement

Bulk electrolysis experiments were performed for the HT-Ni SAC to evaluate its stability and FE for H₂O₂ production. A catalyst ink was drop-cast onto both sides of the carbon paper electrode (SIGRACET[®] GDL 22BB, SGL carbon, 1 × 1 cm²). An H-type electrochemical cell was assembled, in which the working and counter compartments were separated by a Nafion 115 membrane (DuPont). Prior to use, the membrane was pre-treated with 5% H₂O₂ at 80 °C for 1 h. CA measurements were conducted at a constant potential of 0.5 V (vs. RHE) with a continuous O₂ bubbling into the working electrolyte.

The concentration of H₂O₂ produced during bulk electrolysis was quantified by iodometric titration. After completion of the CA test, the electrolyte in the working compartment was thoroughly purged with N₂ to remove dissolved O₂. A known volume of the electrolyte sample and 1 M H₂SO₄ were transferred to a 20 mL glass vial, followed by the addition of 2% KI and molybdate solution ((NH₄)₆Mo₇O₂₄·4H₂O, NH₄NO₃, and aqueous ammonia). The solution immediately turned yellow orange due to formation of I₂ according to reaction (4):



The generated I₂ was titrated immediately with a standardized 0.01 N Na₂S₂O₃ solution following reaction (5).



When the solution color changed from yellow to pale yellow, a 1% starch indicator solution was added, producing a deep blue color. The titration was continued with 0.01 N Na₂S₂O₃

solution until the blue color completely disappeared. The amount of H₂O₂ (in moles) was calculated from the total volume of 0.01 N Na₂S₂O₃ solution consumed, as given by equation (6):

$$\text{Generated H}_2\text{O}_2 \text{ (mol)} = \frac{0.01 \times V(\text{Na}_2\text{S}_2\text{O}_3)}{2} \quad (6)$$

The FE of H₂O₂ production was calculated using equation (7):

$$\text{FE (\%)} = \frac{\text{Generated amount of H}_2\text{O}_2}{\text{Theoretical amount of H}_2\text{O}_2} \quad (7)$$

The theoretical amount of H₂O₂ (in moles) was determined from the total charge passed during CA according to equation (8):

$$\text{Theoretical amount of H}_2\text{O}_2 = \frac{\int i \, dt}{2 \times F} \quad (8)$$

Ni turnover frequency calculation

To evaluate the intrinsic activity of the Ni active sites in X–Ni SACs, the Ni TOF was calculated using equation (9):

$$\text{Ni TOF (s}^{-1} \text{ Ni atom}^{-1}) = \frac{|i_{k,\text{Ni}}| \text{ (A)} \times N_A}{2 \times F \times m \text{ (g)} \times SD \text{ (sites g}^{-1})} \quad (9)$$

where $i_{k,\text{Ni}}$, N_A , F , m , and SD denote the disk kinetic current associated with Ni active sites, Avogadro's number, Faraday constant, catalyst loading on the disk, and active Ni site density, respectively.

The value of $i_{k,\text{Ni}}$ was determined using SCN[−] poisoning experiments conducted in a 0.1 M KOH electrolyte containing 10 mM KSCN. ORR measurements were performed following the same protocol as described above, except that the Pt ring current was not monitored because

SCN⁻ ions can poison Pt ring, rendering the ring current unreliable. The $i_{k,Ni}$ was obtained from equation (10):

$$|i_{k,Ni}| \text{ (A)} = |i_{k,d}| \text{ (A)} - |i_{k,d_SCN^-}| \text{ (A)} \quad (10)$$

where $i_{k,d}$ and i_{k,d_SCN^-} represent the disk kinetic currents before and after the SCN⁻ poisoning, respectively.

The *SD* of *X*-Ni SACs was quantified using CN⁻ poisoning experiments following a previously reported method⁴⁶. The *SD* value was calculated from the change in CN⁻ concentration in the electrolyte (ΔC_{CN^-}), determined by UV-vis spectroscopy (Genesis 400, Thermo Fisher Scientific), in combination with the relative decrease in ORR activity ($\Delta i/i_{pristine}$). Their relationship is described by equation (11):

$$SD \text{ (sites g}^{-1}\text{)} = \frac{\Delta C_{CN^-} \text{ (mol L}^{-1}\text{)} \times V \text{ (L)} \times N_A}{m_{cat} \text{ (g)} \times \Delta i/i_{pristine}} \quad (11)$$

where V and m_{cat} denote the electrolyte volume and the mass of catalyst used in the experiment, respectively.

Bias-free co-production of H₂O₂ and Cl₂ with electrodialysis

To achieve bias-free co-production of the H₂O₂ and Cl₂ with simultaneous electrodialysis, the PV-SAEC system cell was constructed. The Pt SAC anode was prepared by drop-casting of catalyst ink onto a hydrophobic carbon paper (1 × 1 cm²), whereas the HT-Ni SAC cathode was fabricated by depositing the catalyst ink onto a gas diffusion electrode (GDE, 1 × 1 cm²). The two-electrode PV-SAEC system comprised three electrolyte compartments (0.1 M HClO₄ + 1.0 M NaCl || 1.0 M NaCl || 1.0 M NaOH) separated by two types of membranes: AEM (AXP-D) and NASICON. The Pt SAC electrode was immersed in the acidic chloride electrolyte (0.1 M HClO₄ + 1.0 M NaCl), while the HT-Ni SAC electrode was placed in the 1.0 M NaOH solution.

The PV component consisted of three Si solar cells connected in series, which were directly coupled to the electrochemical cell to form the PV-SAEC system. A 300 W xenon lamp was used as the light source, and all experiments were performed under simulated 1 sun illumination. Product accumulation experiments for H₂O₂ and Cl₂ were conducted in a closed system, whereas long-term stability and desalination performance were evaluated using a flow-cell configuration. The concentration of H₂O₂ was quantified using the DPD–POD colorimetric method⁵⁰. Specifically, a mixture of 0.1 M phosphate buffer solution (PBS; Na₂HPO₄ and NaH₂PO₄), analyte, DPD solution (DPD in 0.1 N H₂SO₄), and POD solution was prepared. After color development, the H₂O₂ concentration was determined from the absorbance at 551 nm using a UV–vis spectrophotometer (Shimadzu). The amount of Cl₂ produced was detected by iodometric titration¹². The analyte was mixed with 0.1 M KI solution and a few drops of starch indicator, leading to the formation of blue complex. The solution was then titrated with a standardized 0.01 M Na₂S₂O₃ until the color disappeared. The amount of generated Cl₂ were calculated using equation (12):

$$\text{Generated } Cl_2 \text{ (mol)} = \frac{C(\text{Na}_2\text{S}_2\text{O}_3) \times V(\text{Na}_2\text{S}_2\text{O}_3)}{2} \quad (12)$$

Data Availability

The data supporting this study are available from the corresponding author upon reasonable request.

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Author contributions

S.H.J. supervised the project. S.H.J., J.-W.J., T.H.O., C.H.C., J.S.L., J.C., S.H., and G.B. conceived and designed the experiments and calculations. J.S.L. carried out catalyst synthesis, materials characterizations, and electrochemical analyses with the help of J.K. and H.R.S. G.B. performed Ni site density calculations and analysis. J.C. and J.N. constructed PV-SAEC system and conducted experiments on the co-production of H₂O₂ and Cl₂ with desalination. S.H. and M.S.K. evaluated TEA–LCA of PV-SAEC system. S.J., H.Y.J. and J.K. contributed to TEM analysis. K.I., H.-G.L. and T.J.S. conducted NEAXFS measurements and analysis. Y.J.S., and B.S. provided critical feedback on the manuscript. J.S.L., J.C., S.H., G.B., C.H.C., J.-W.J., T.H.O., and S.H.J. co-wrote the manuscript. All authors contributed to the discussion, and finalization of the documents.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to S.H.J., J.-W.J., T.H.O., and C.H.C.

Competing interests

The authors declare no completing interests.

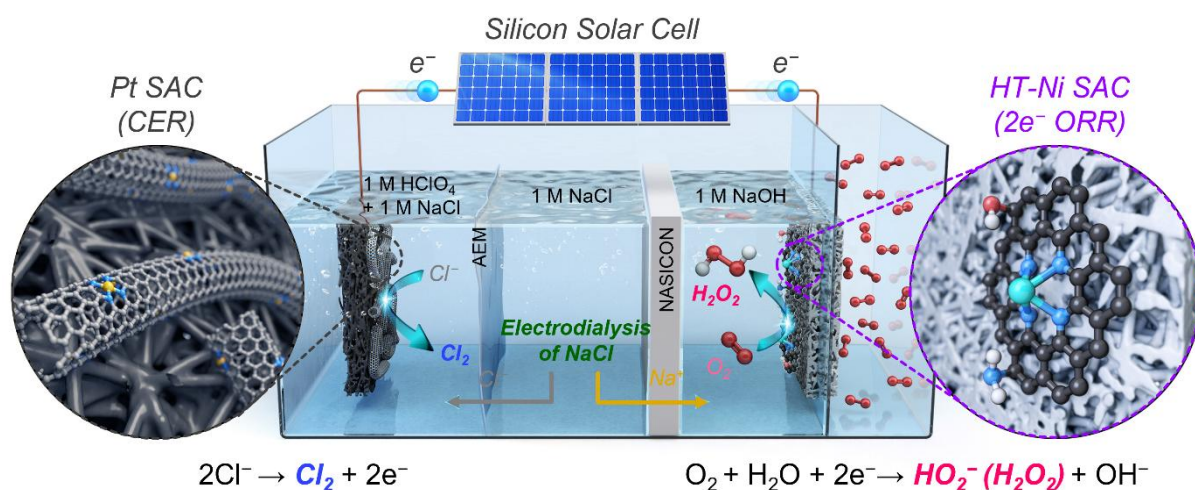


Fig. 1 | Schematic illustration for the PV-SAEC system. Bias-free co-electrosynthesis of H_2O_2 and Cl_2 enabled by an HT-Ni SAC cathode and a Pt SAC anode, integrated with electrodesalination-based desalination.

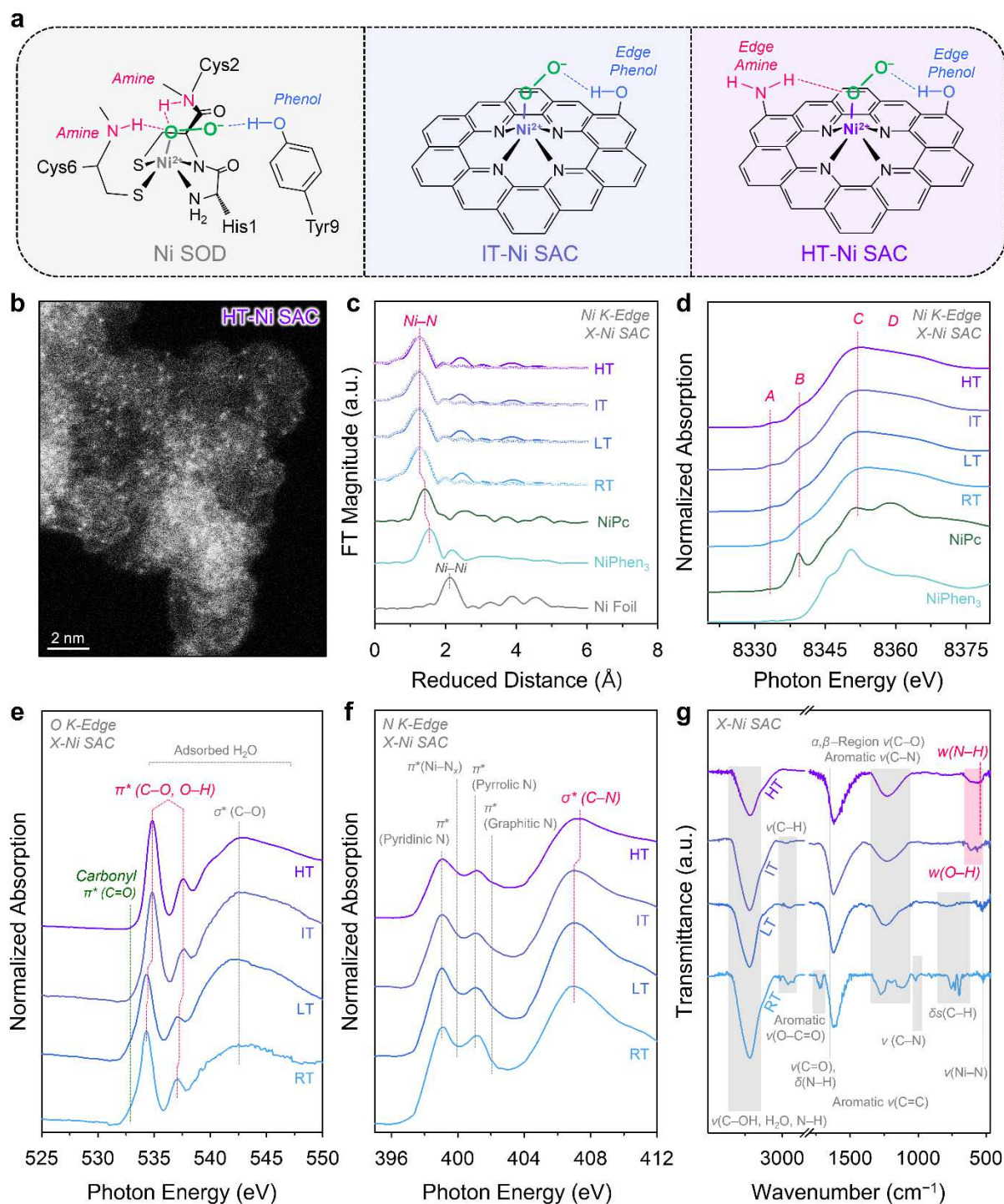


Fig. 2 | Structural and spectroscopic characterization of X-Ni SACs. **a**, Cofactor structure of Ni SOD and the proposed local coordination structures of IT- and HT-Ni SACs. **b**, HAADF-STEM image of HT-Ni SAC. **c**, k^3 -weighted EXAFS spectra of X-Ni SACs, Ni foil, NiPc, and NiPhen₃. **d**, Ni K-edge XANES spectra of X-Ni SACs, NiPc, and NiPhen₃. **e-g**, O K-edge NEXAFS (**e**), N K-edge NEXAFS (**f**), and FT-IR (**g**) spectra of X-Ni SACs.

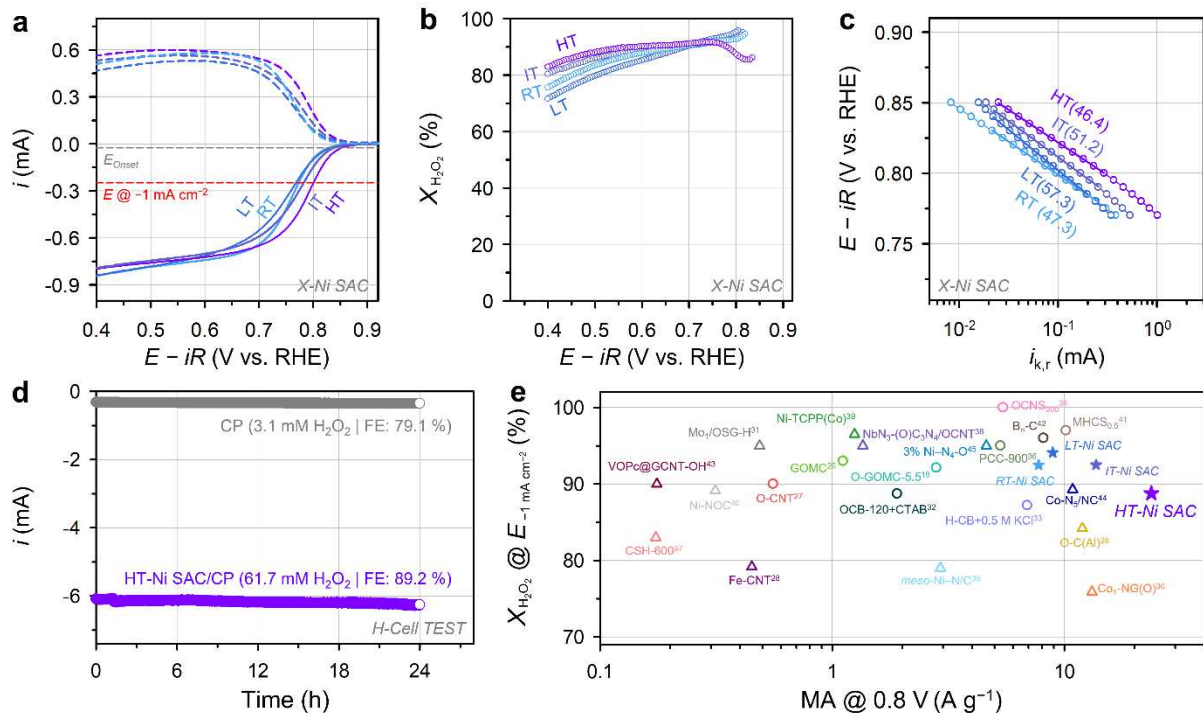


Fig. 3 | Electrochemical $2e^-$ ORR performance of X-Ni SACs. **a,b**, ORR LSV curves (**a**) and corresponding H_2O_2 selectivity (**b**) of X-Ni SACs measured in O_2 -saturated 0.1 M KOH. **c**, Tafel plots of X-Ni SACs. Values in parentheses denote Tafel slopes (mV dec^{-1}). **d**, Bulk electrolysis of HT-Ni SAC measured in an H-type electrochemical cell at 0.5 V (vs. RHE) in O_2 -saturated 0.1 M KOH over 24 h. **e**, Benchmark comparison highlighting the mass activity at 0.8 V (vs. RHE) and H_2O_2 selectivity at a current density of -1 mA cm^{-2} of X-Ni SACs (stars) relative to reported SACs (triangles) and carbon-based catalysts (circles). The numbers refer to the corresponding references.

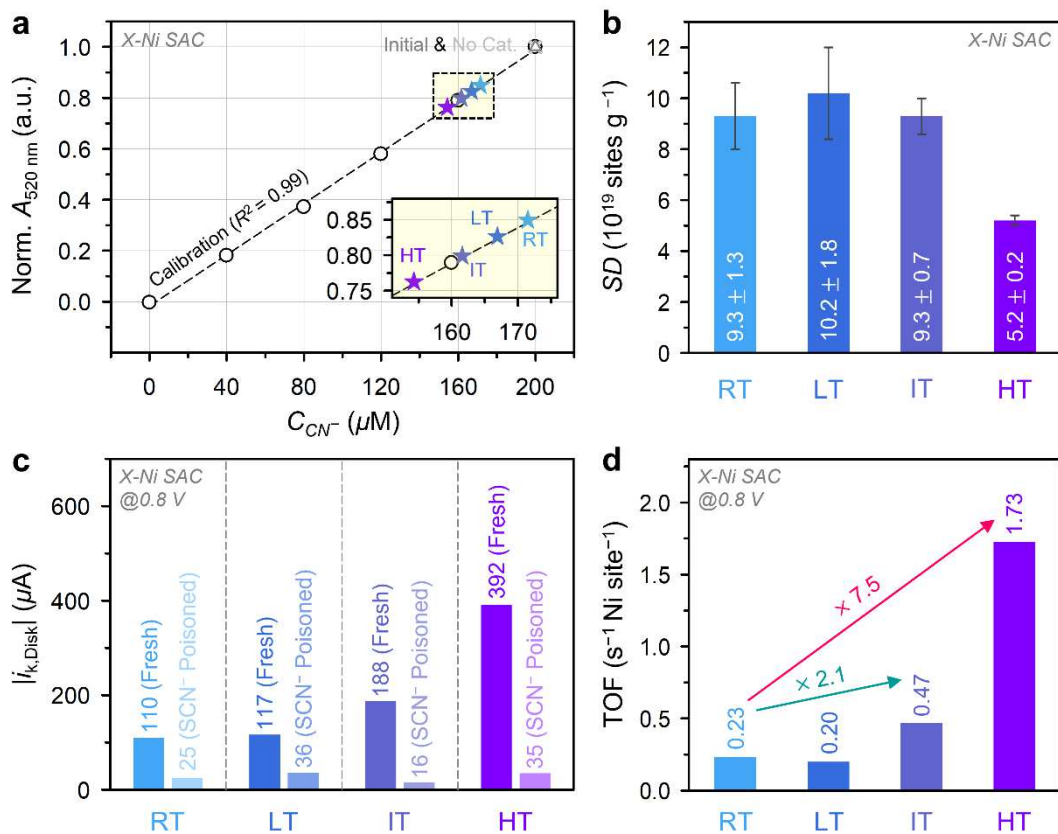


Fig. 4 | Determination of Ni TOF for X-Ni SACs. **a**, Quantification of CN^- concentration by UV-vis spectroscopy before and after CN^- poisoning of the X-Ni SACs surface. **b**, Surface-exposed SD of X-Ni SACs derived from CN^- titration. **c**, Kinetic ORR currents of X-Ni SACs measured before and after SCN^- poisoning, confirming the Ni single-atom sites as the dominant active centers. **d**, Intrinsic TOF of X-Ni SACs for H_2O_2 production normalized to the number of Ni single-atom sites.

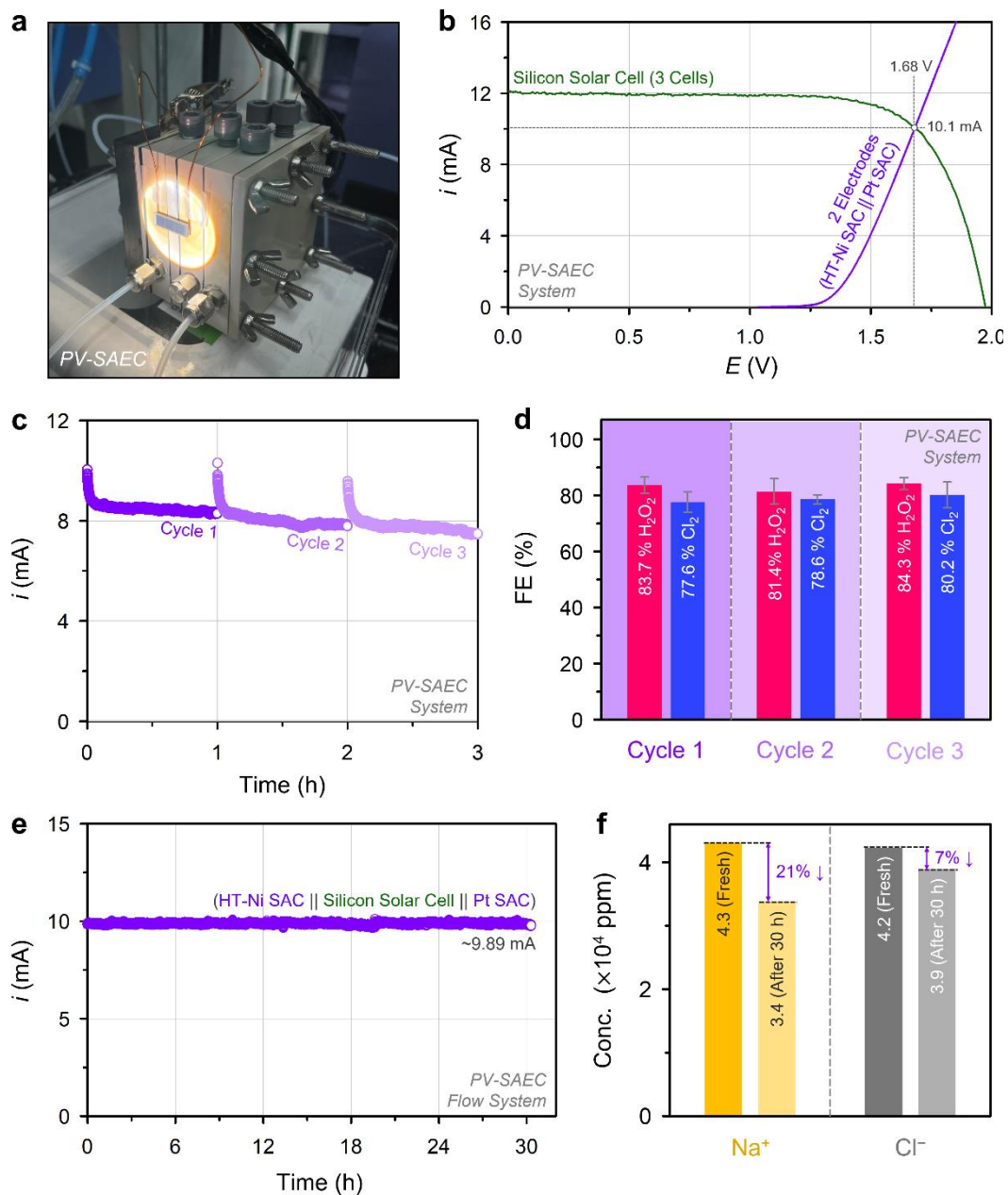


Fig. 5 | Bias-free co-production of Cl_2 and H_2O_2 with desalination in the PV-SAEC system. **a**, Photograph of the assembled PV-SAEC cell integrating the HT-Ni SAC cathode and the Pt SAC anode. **b**, Polarization curves of the PV module under 1 sun illumination and the two-electrode SAEC (HT-Ni SAC/GDL || Pt SAC/hydrophobic CP). **c**, CA response of the PV-SAEC system operated in a closed configuration under bias-free conditions (0 V) over three consecutive 1h cycles. **d**, FE efficiencies for H_2O_2 and Cl_2 during each electrolysis cycle. **e**, Long-term operational stability of the PV-SAEC system operated in flow-cell configuration over 30 h. **f**, Na^+ and Cl^- concentration in the NaCl solution in desalination compartment before and after 30 h operation, demonstrating simultaneous electro dialysis-based desalination.

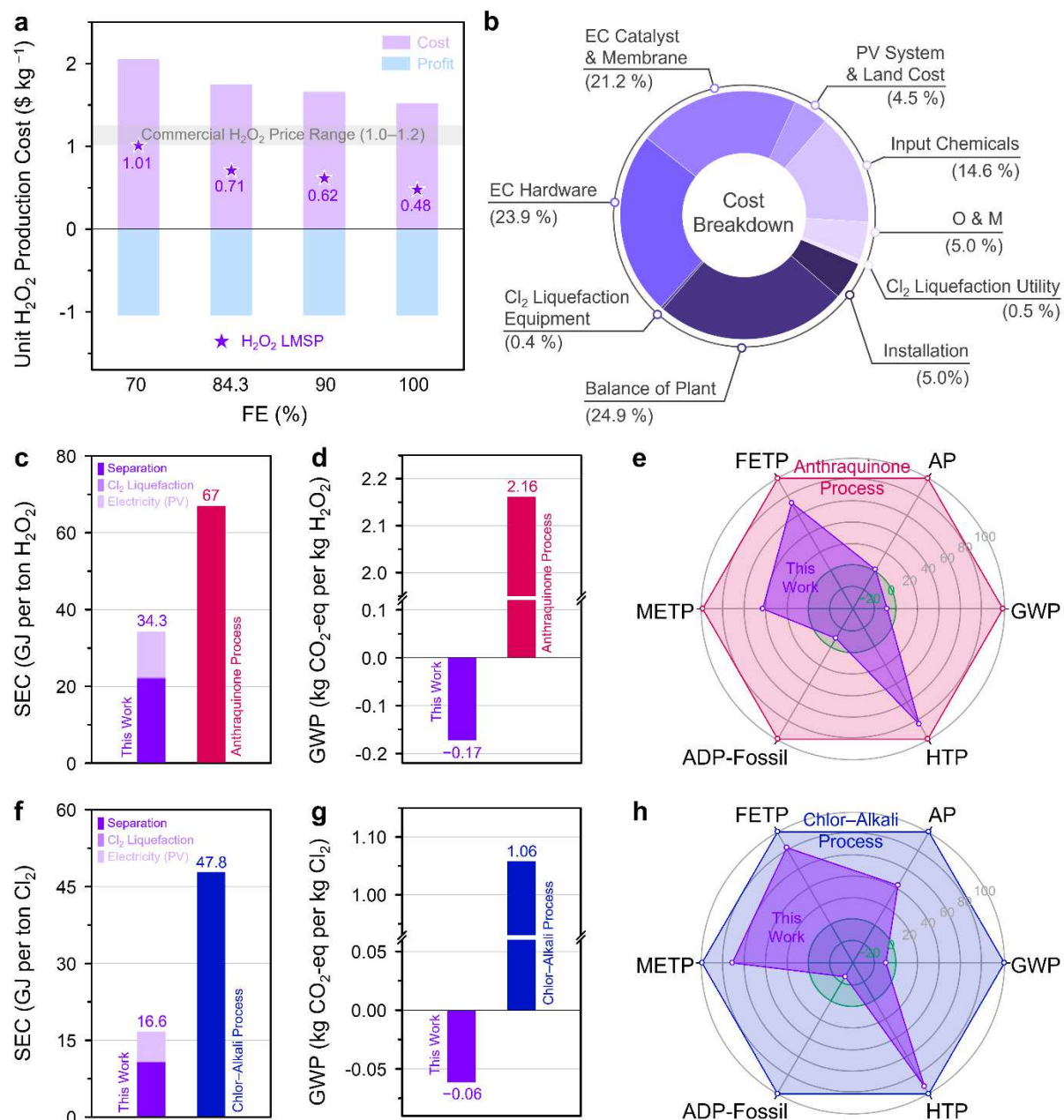


Fig. 6 | TEA–LCA analysis of PV–SAEC system. a, Sensitivity of the levelized H₂O₂ production cost and profitability as a function of FE under the H₂O₂ scenario. **b**, Breakdown of the major CAPEX and OPEX contributions to the unit H₂O₂ production cost. **c–e**, SEC (**c**), GWP (**d**), and selected environmental impact indicators (**e**) of the PV–SAEC system compared with the conventional anthraquinone process. **f–h**, SEC (**f**), GWP (**g**), and selected environmental impact indicators (**h**) of the PV–SAEC system compared with the conventional chlor–alkali process.

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