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(54) **METAL COMPOUND BASED CATALYSTS FOR ELECTROSYNTHESIS OF HYDROGEN PEROXIDE AND LINEAR PAIRED ELECTROCHEMICAL VALORIZATION OF BIOMASS-DERIVED FEEDSTOCKS**

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C25B 11/053 (2006.01)
C25B 11/081 (2006.01)
C25B 15/08 (2006.01)

(52) **U.S. Cl.**
 CPC *C25B 1/30* (2013.01); *C25B 11/053* (2021.01); *C25B 11/081* (2021.01); *C25B 15/087* (2021.01)

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(21) Appl. No.: **18/532,418**

(22) Filed: **Dec. 7, 2023**

Related U.S. Application Data

(60) Provisional application No. 63/430,933, filed on Dec. 7, 2022.

(57) **ABSTRACT**

Disclosed herein is an electrochemical cell comprising an electrolyte and a cathode immersed in the electrolyte, wherein the cathode comprises a two-electron oxygen reduction reaction (2e⁻ ORR) electrocatalyst composed of a metal chalcogenide. Also disclosed are methods for production of hydrogen peroxide or preparing oxidation products of a biomass-derived feedstock with the electrochemical cells described herein.

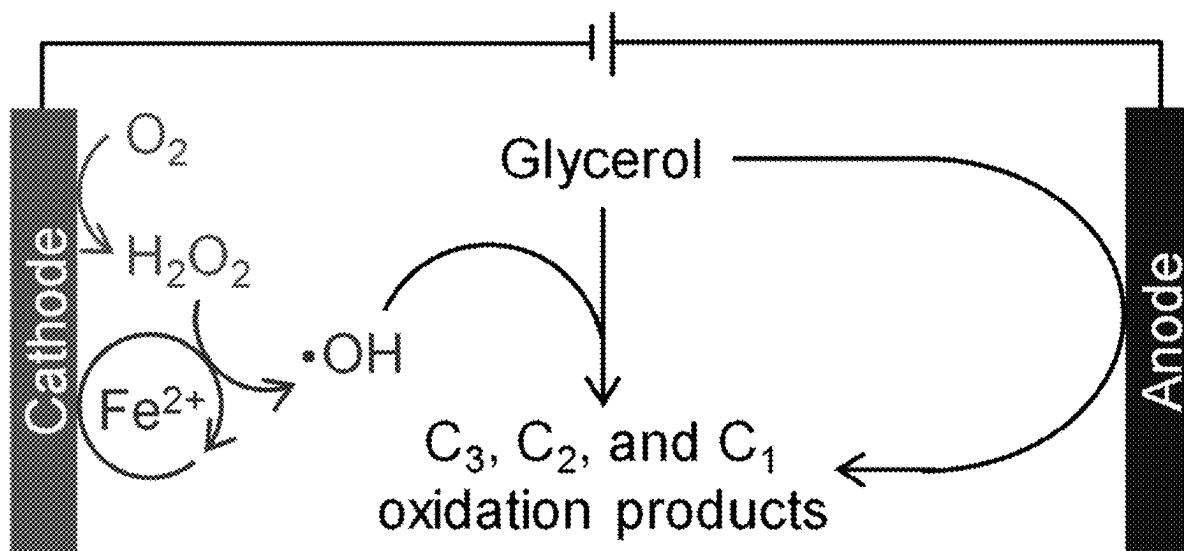


FIG. 1

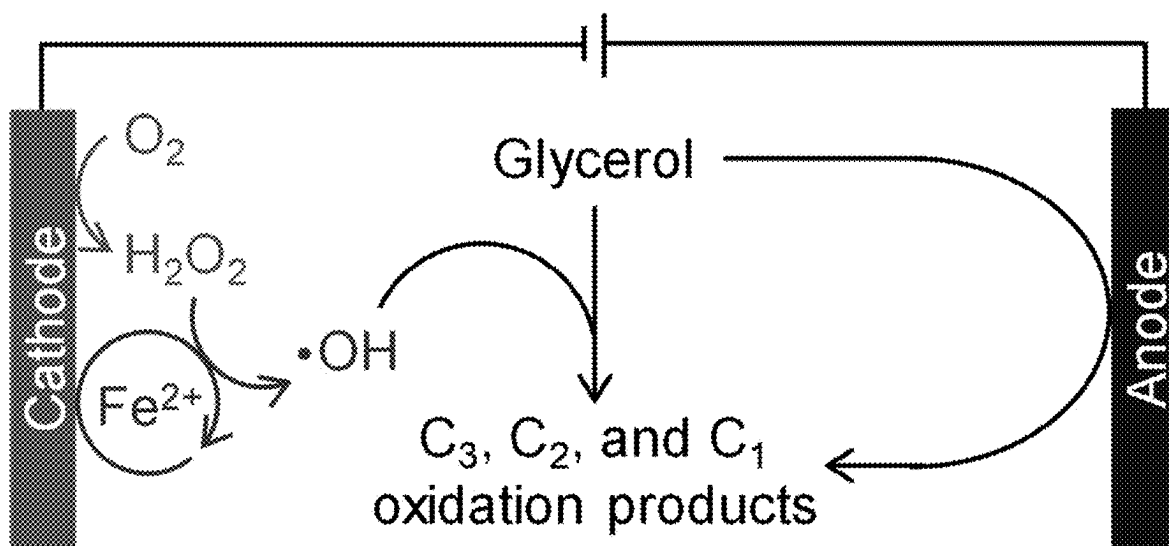


FIG. 2

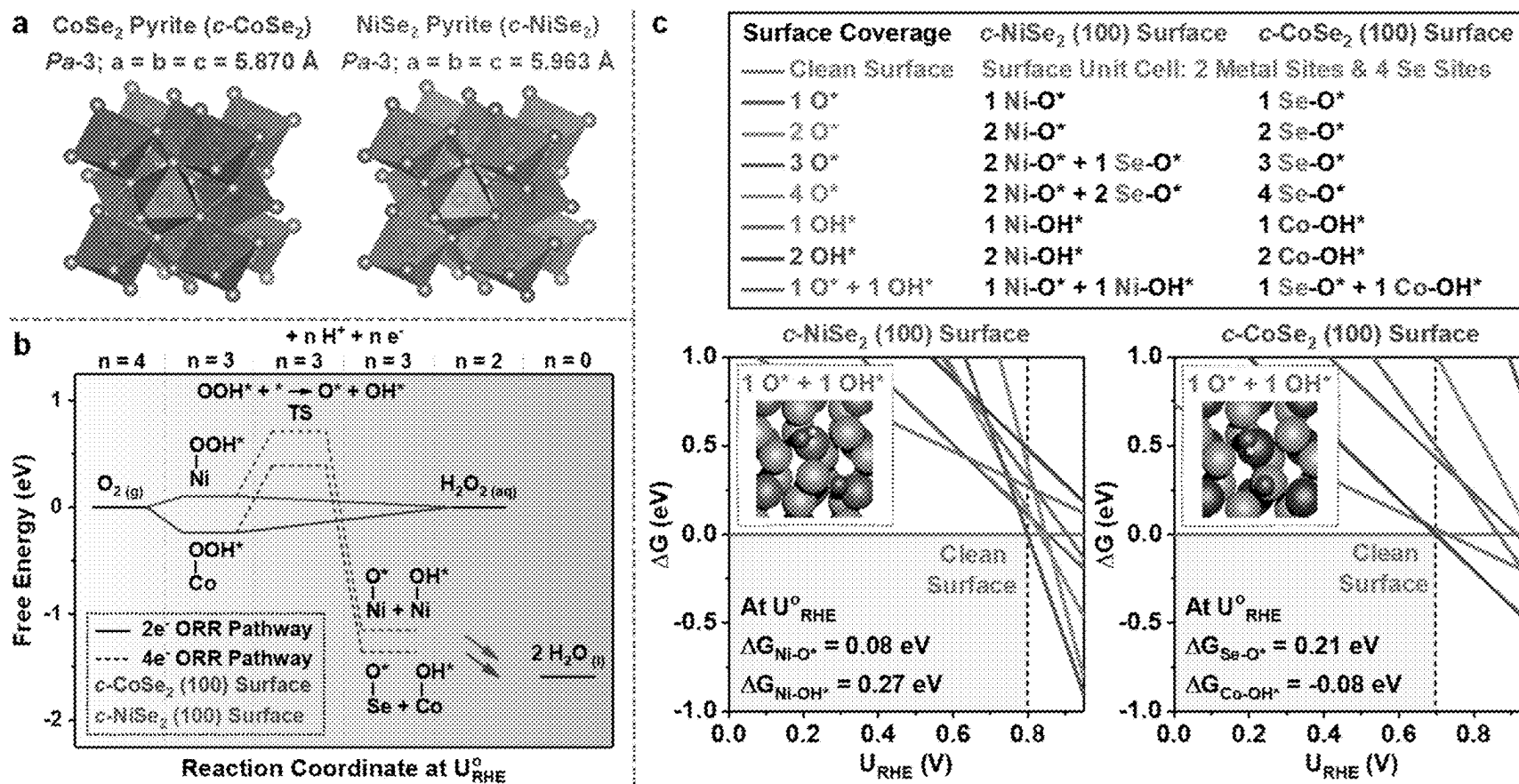


FIG. 3

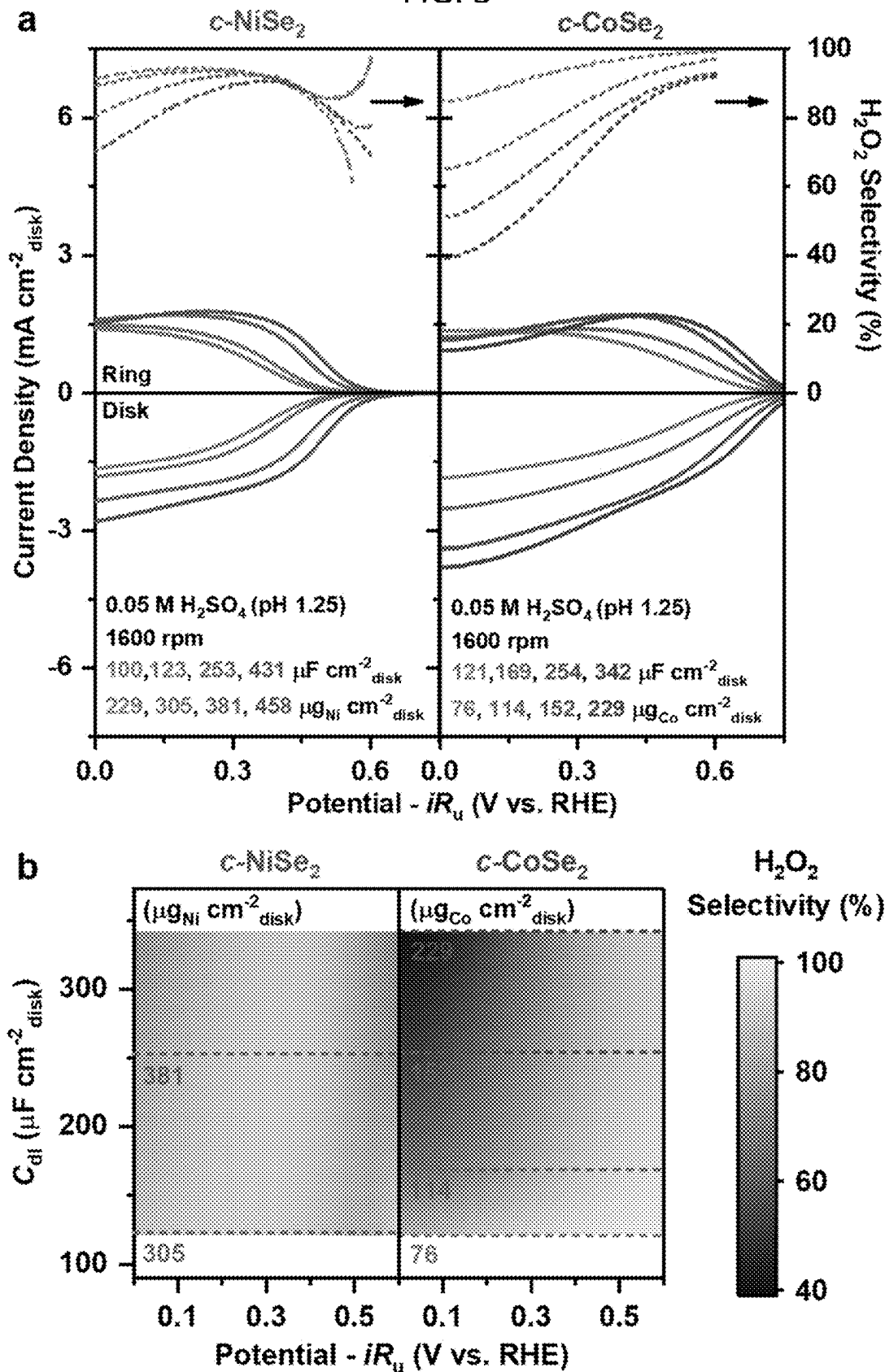


FIG. 3 Continued

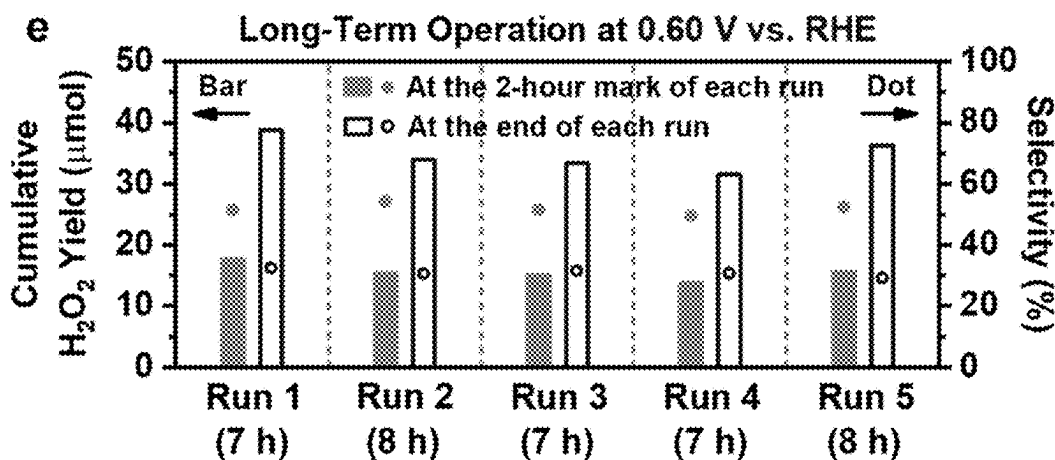
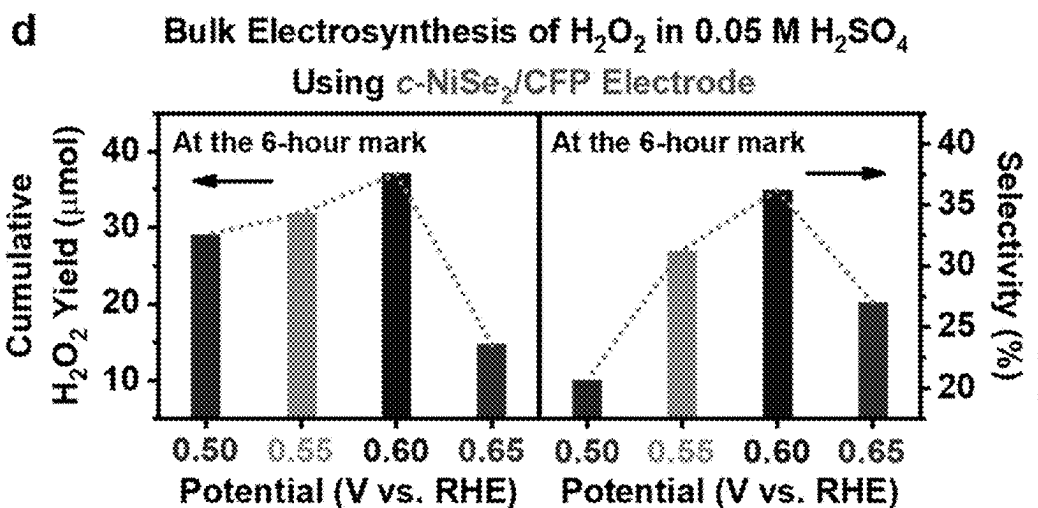
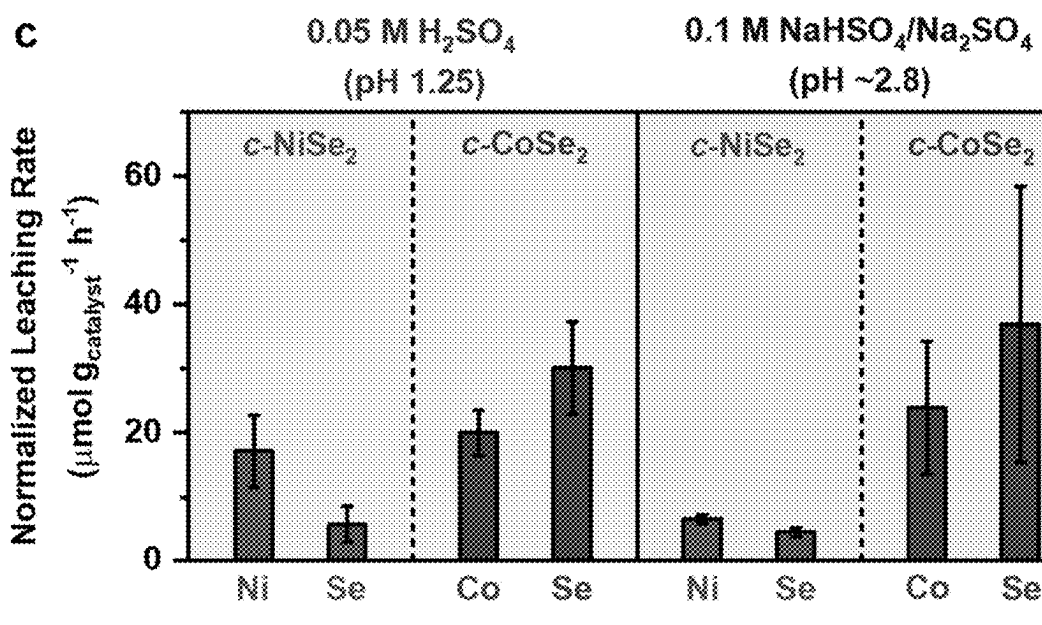


FIG. 4

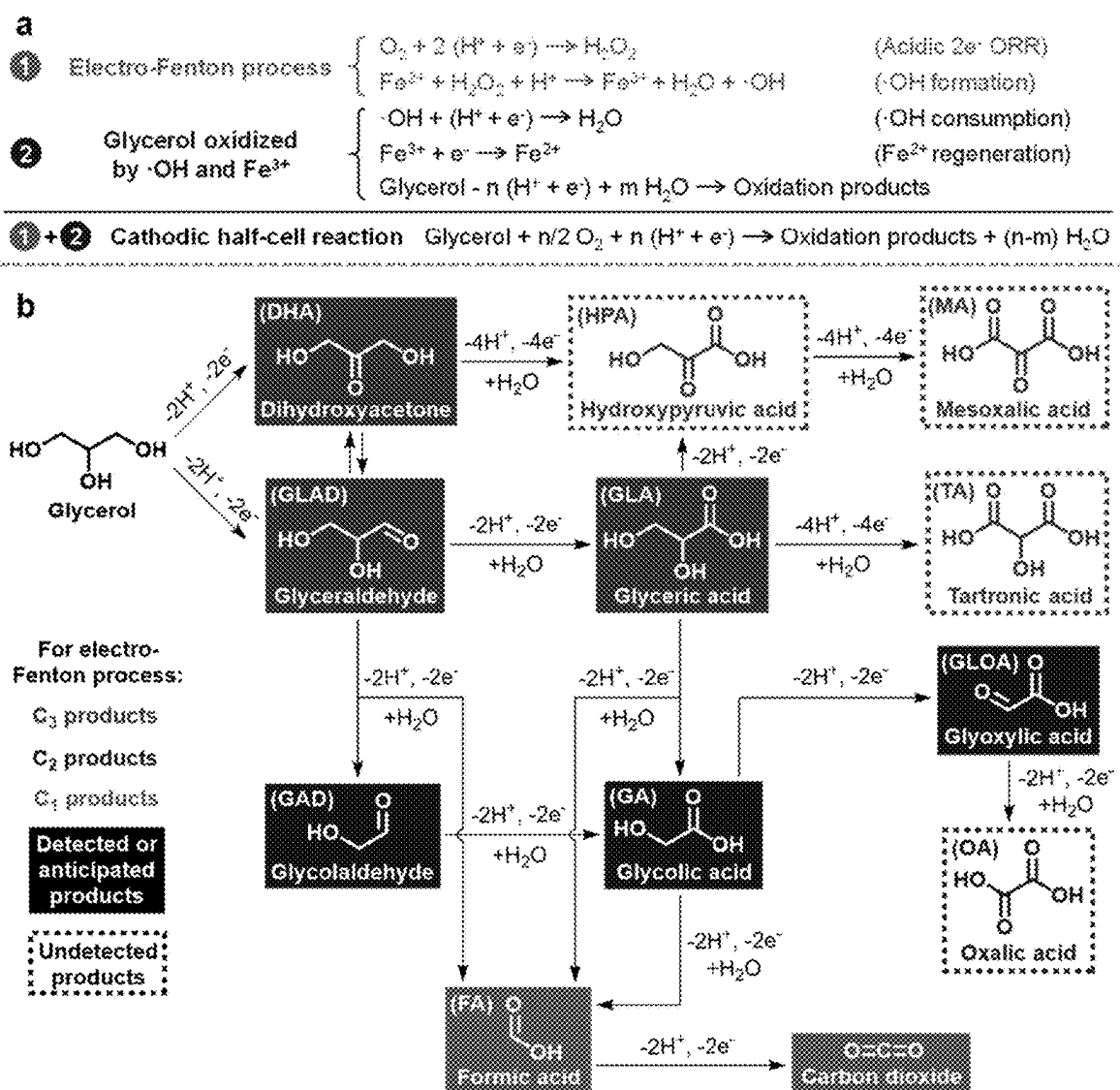


FIG. 5

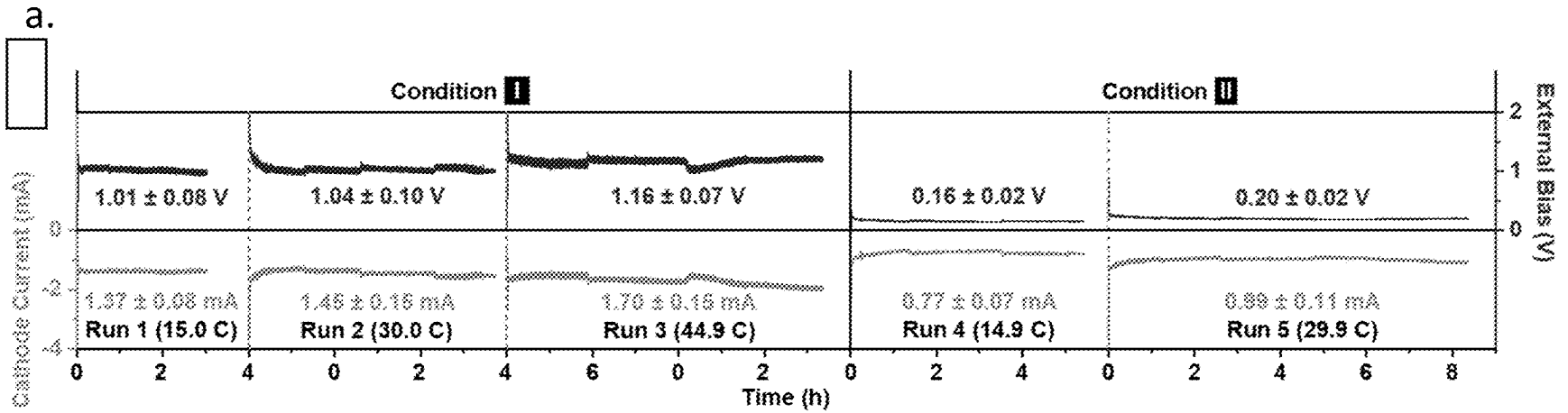


FIG. 5 continued

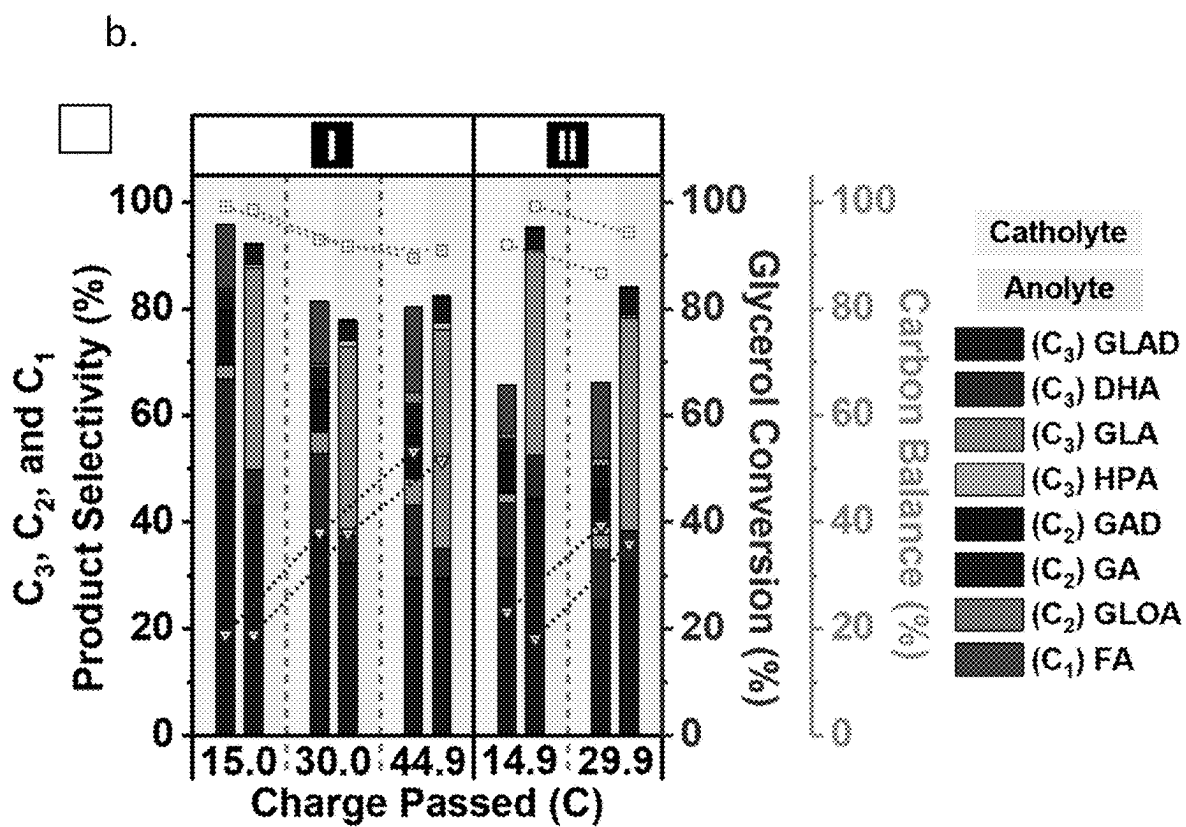
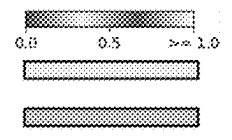
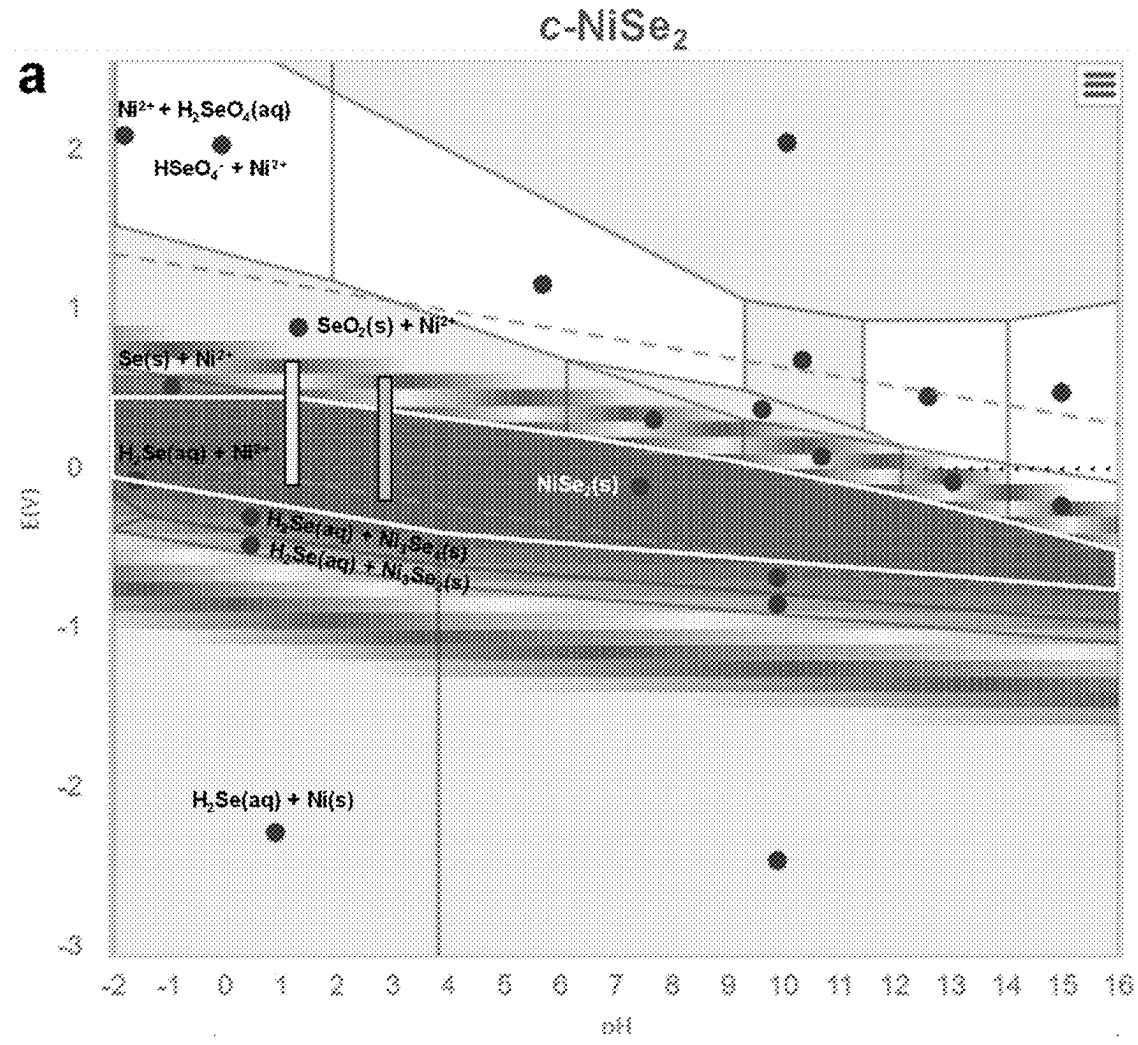


FIG. 6

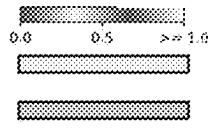
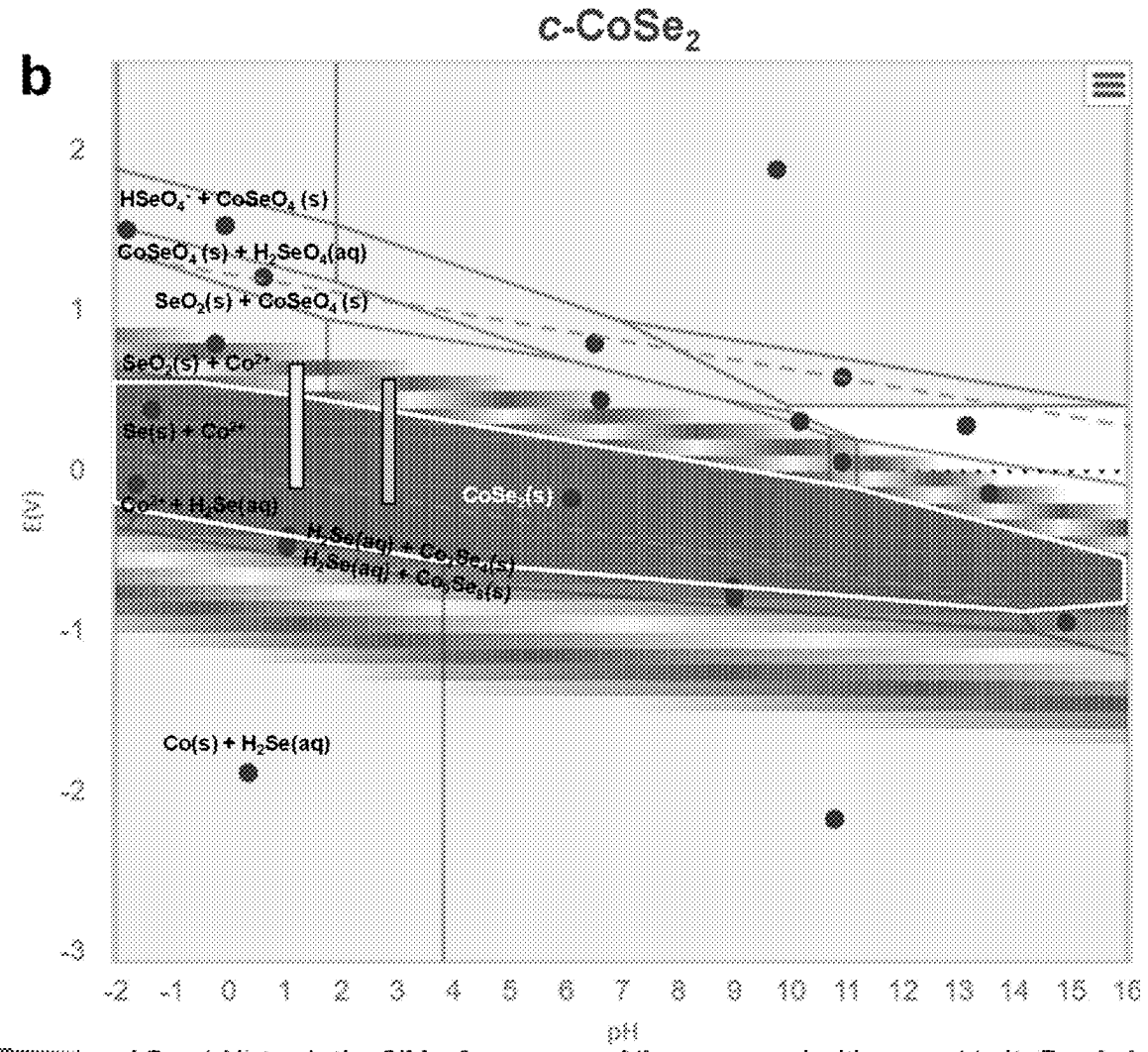


ΔG_{pbx} (eV/atom): the Gibbs free energy of the compound with respect to its Pourbaix stable phase

Potential and pH ranges of interest for the acidic 2e⁻ ORR (-0.025 to 0.75 V vs. RHE; pH 1.25 for 0.05 M H₂SO₄)

Potential and pH ranges of interest for the electro-Fenton process (-0.025 to 0.75 V vs. RHE; pH 2.8 to 3.0)

FIG. 6 Continued



ΔG_{pbx} (eV/atom): the Gibbs free energy of the compound with respect to its Pourbaix stable phase

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Potential and pH ranges of interest for the electro-Fenton process (-0.025 to 0.75 V vs. RHE; pH 2.8 to 3.0)

FIG. 7

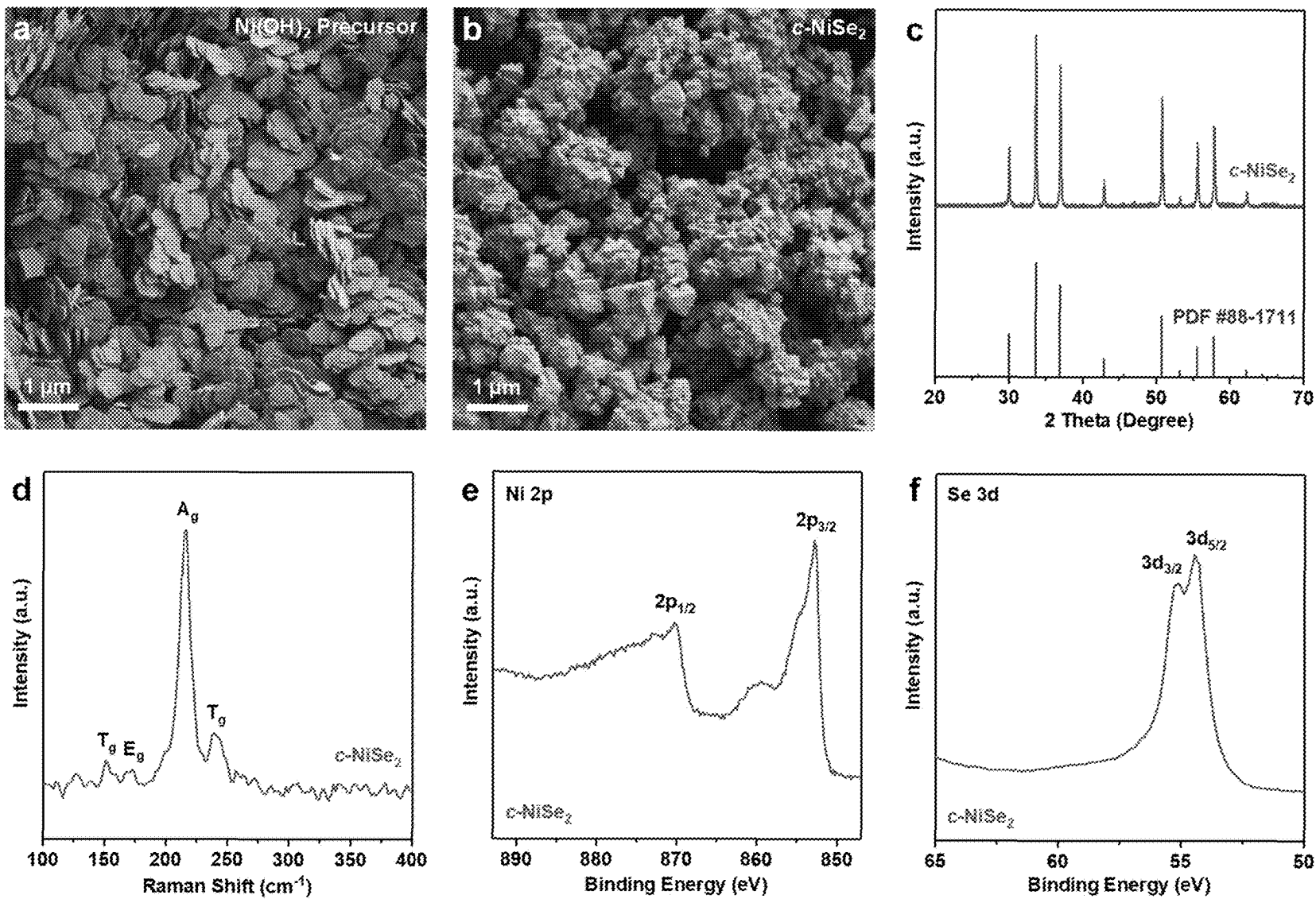


FIG. 8

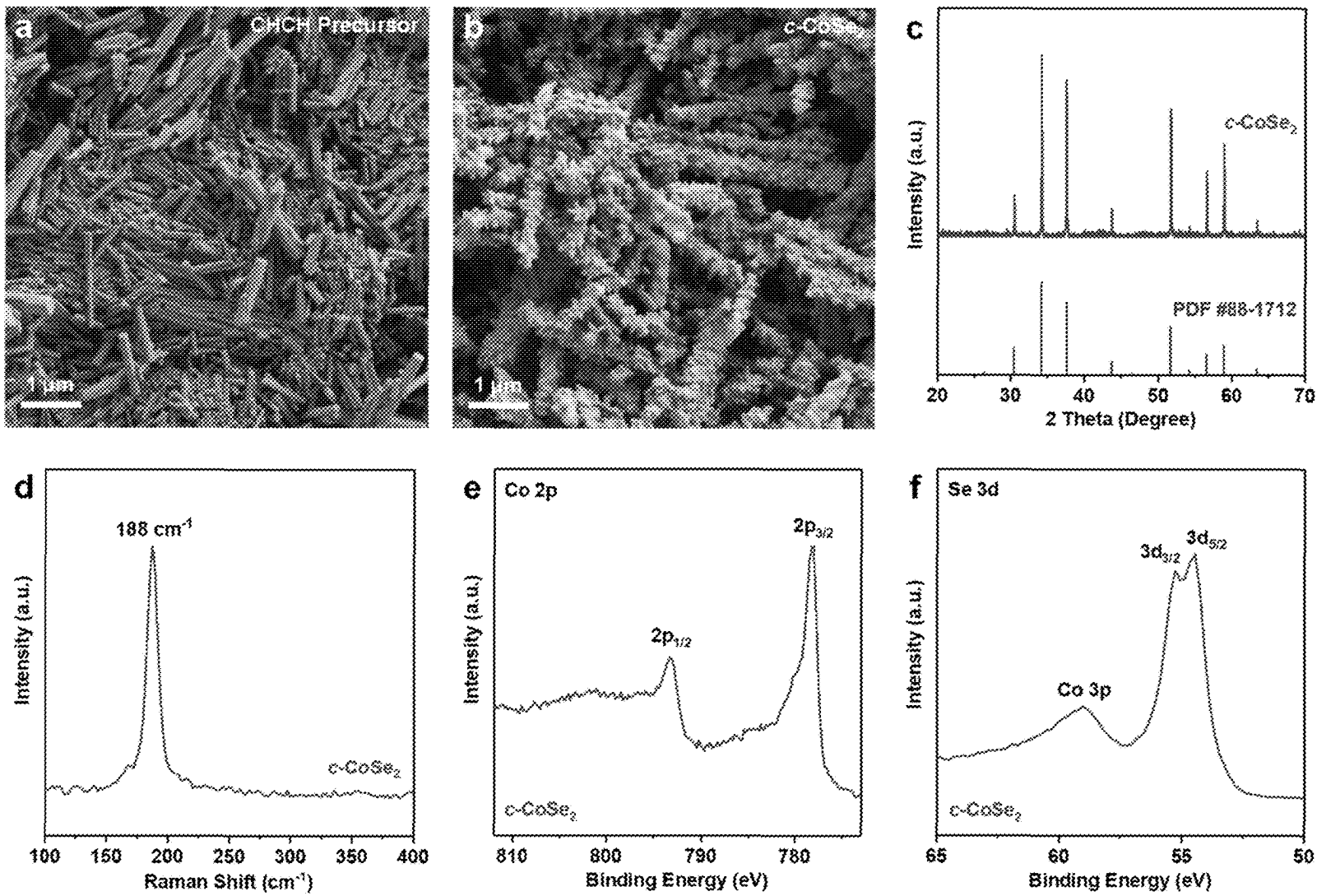


FIG. 9

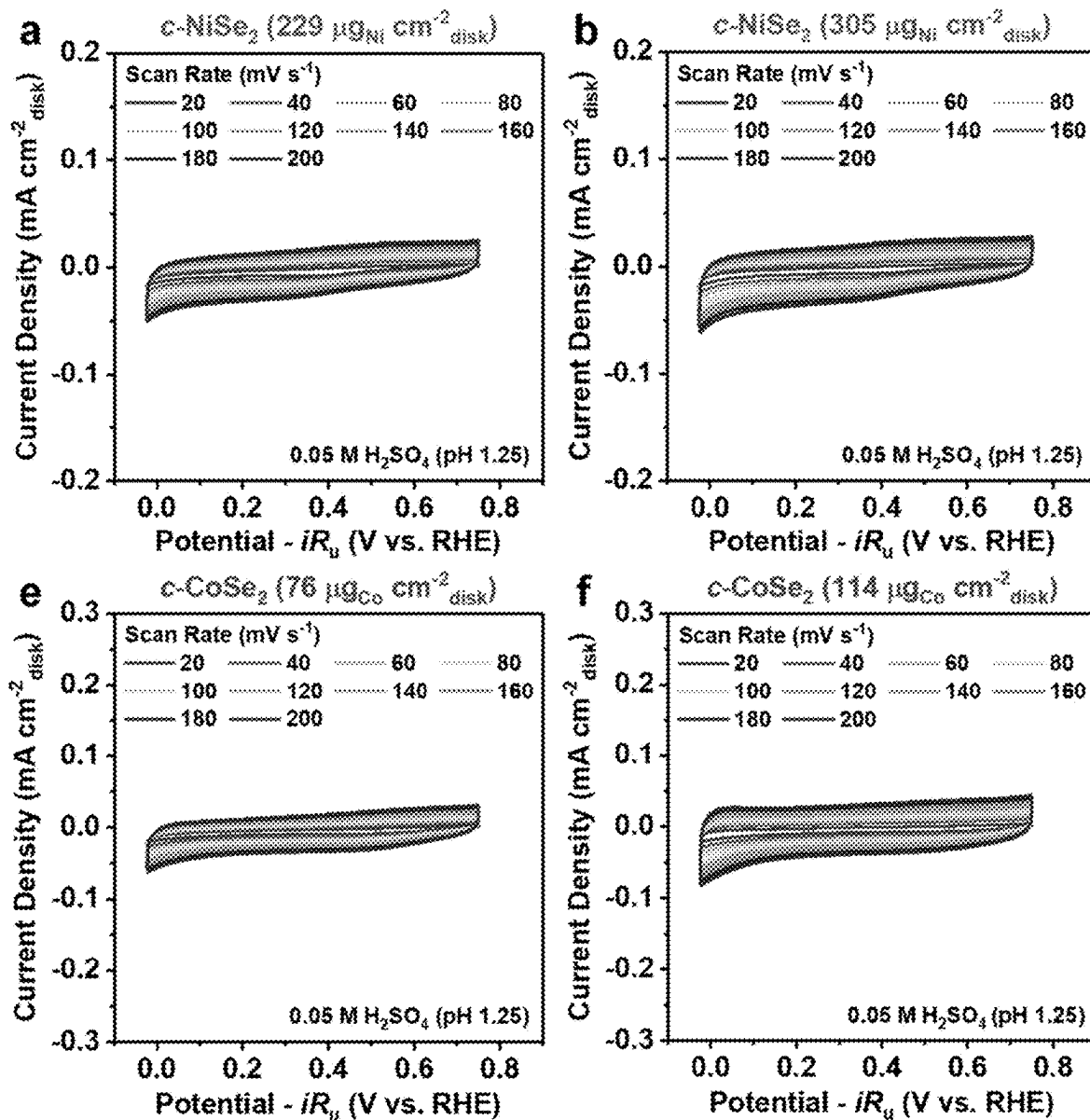
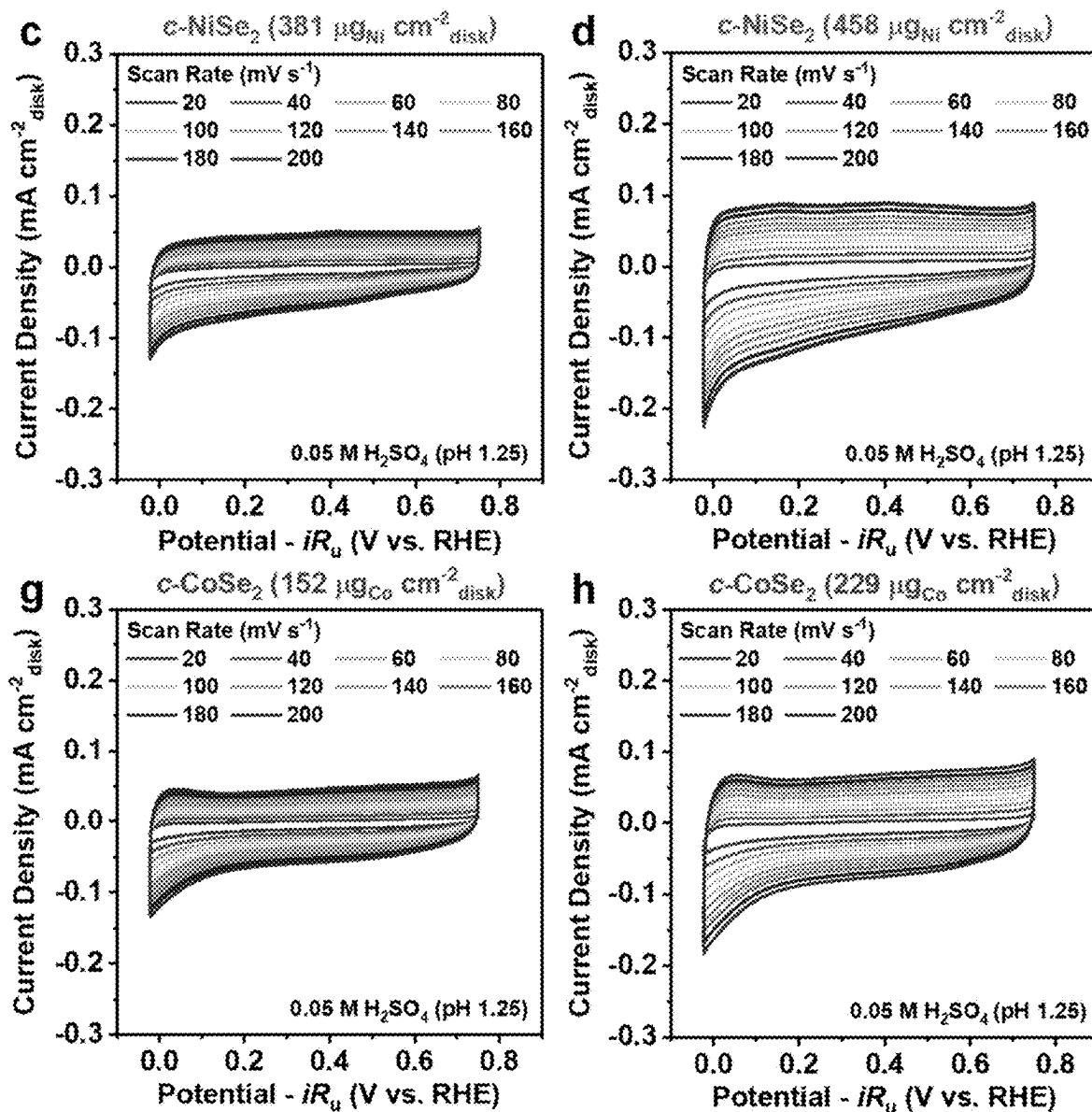


FIG. 9 continued



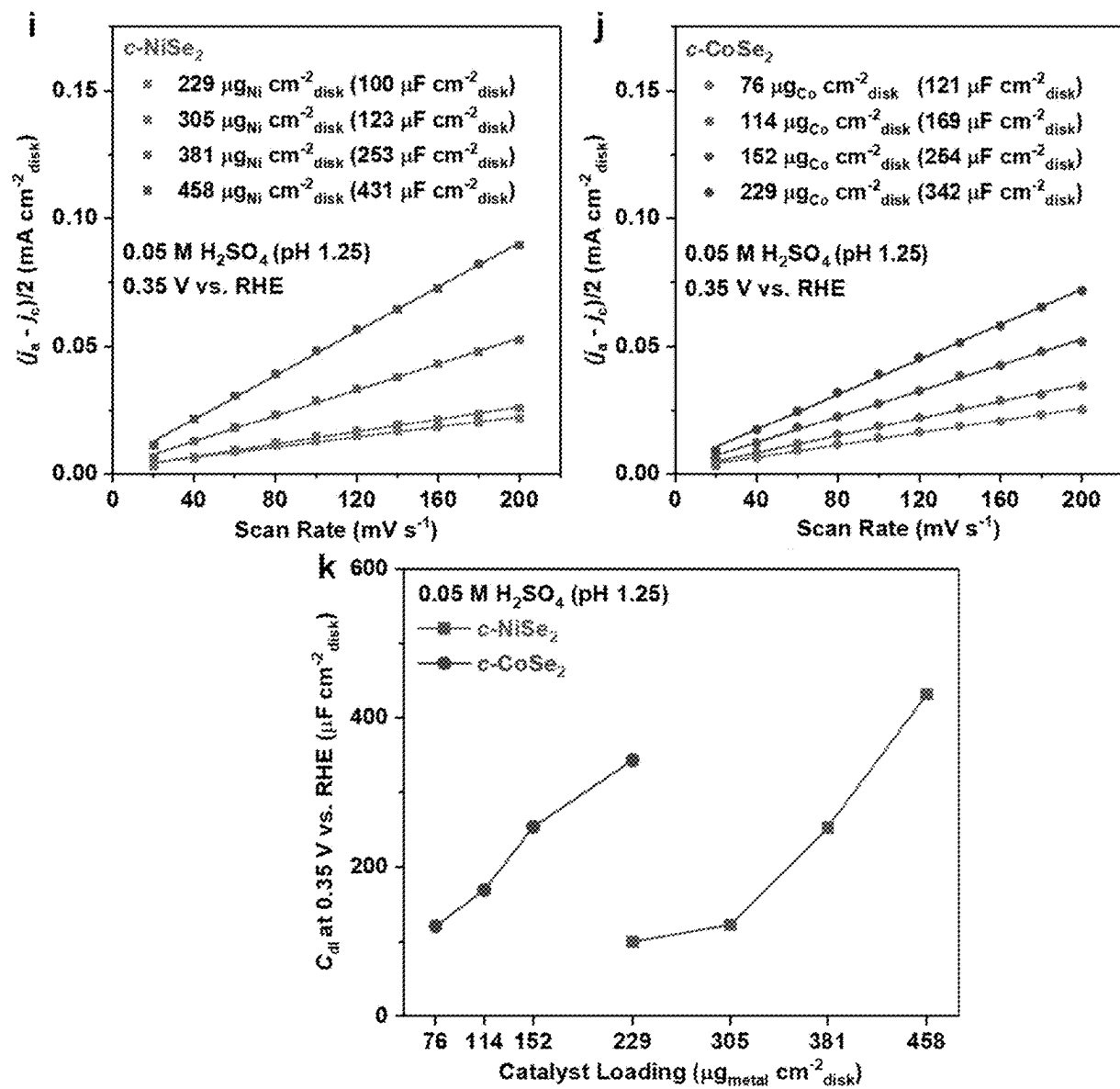


FIG. 9 continued

FIG. 10

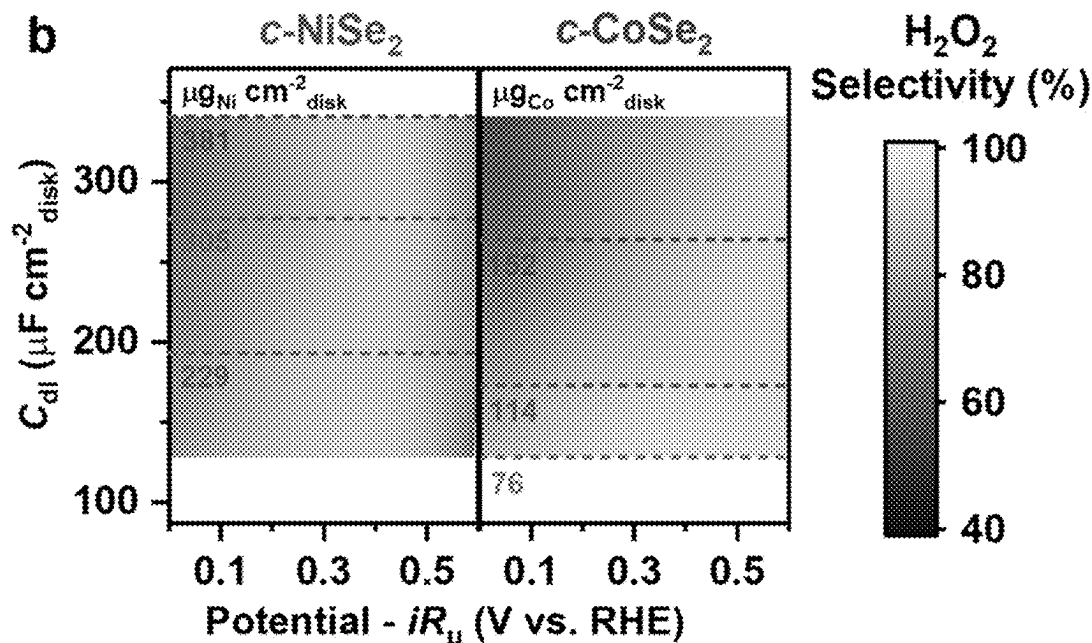
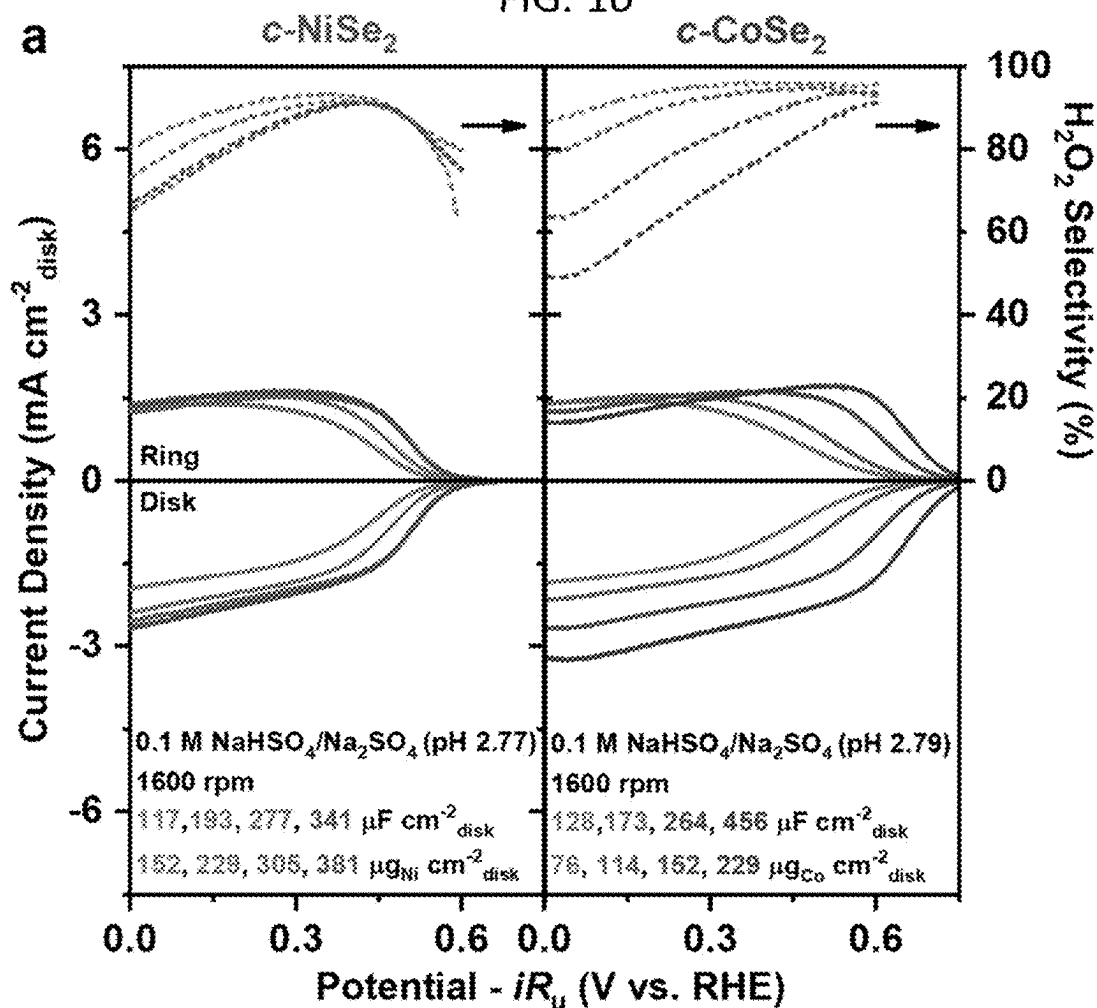


FIG. 11

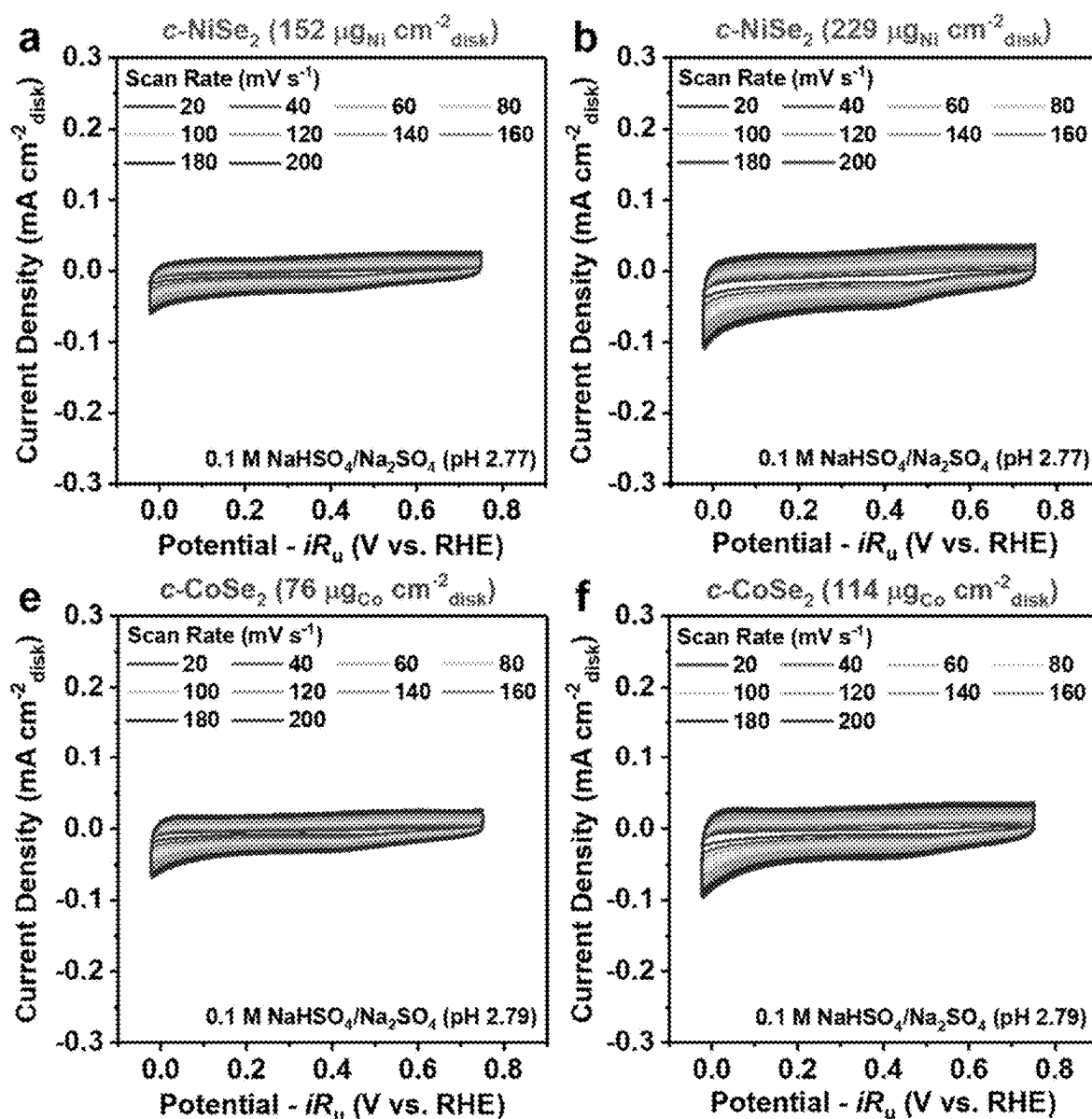
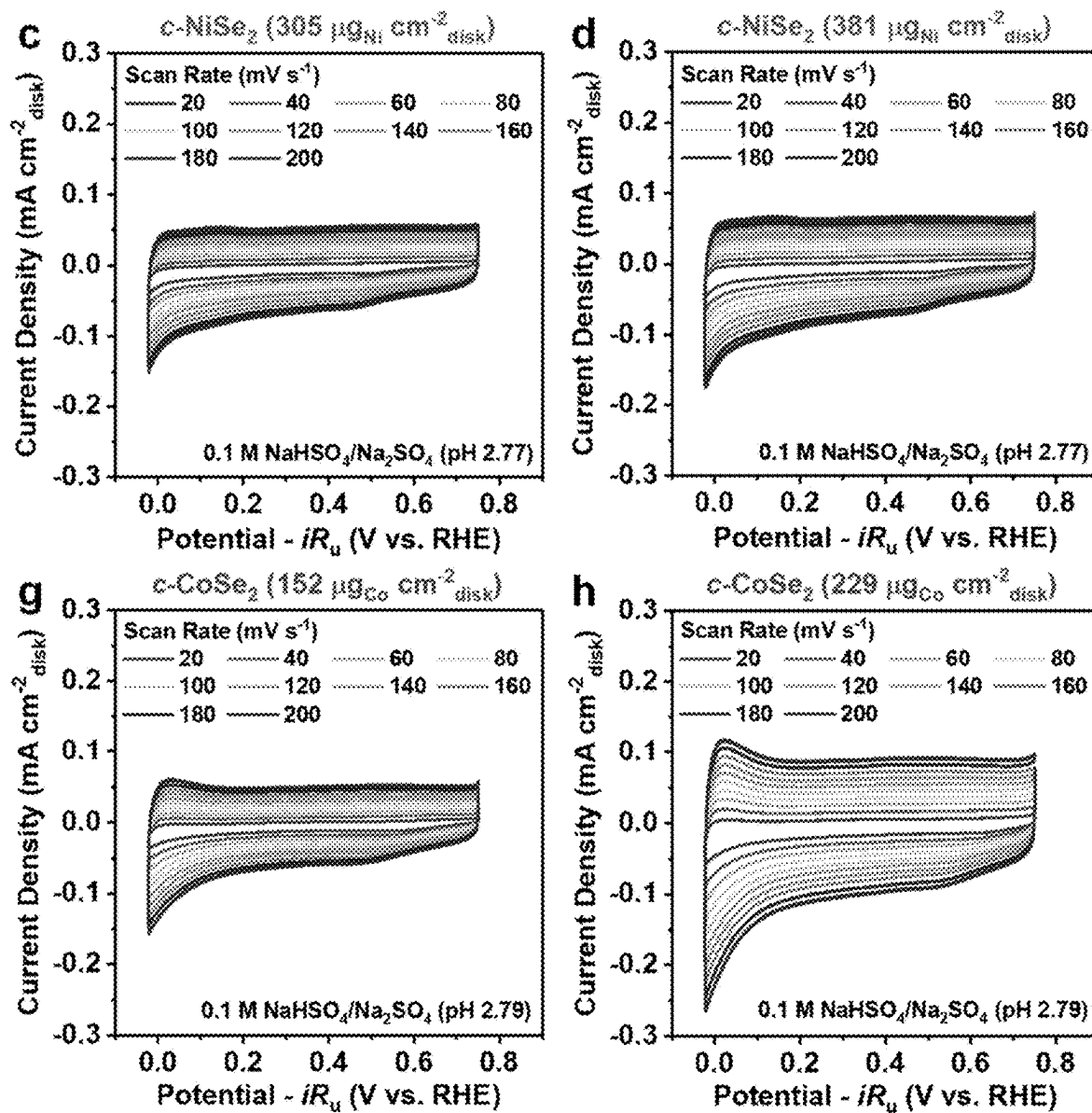


FIG. 11 continued



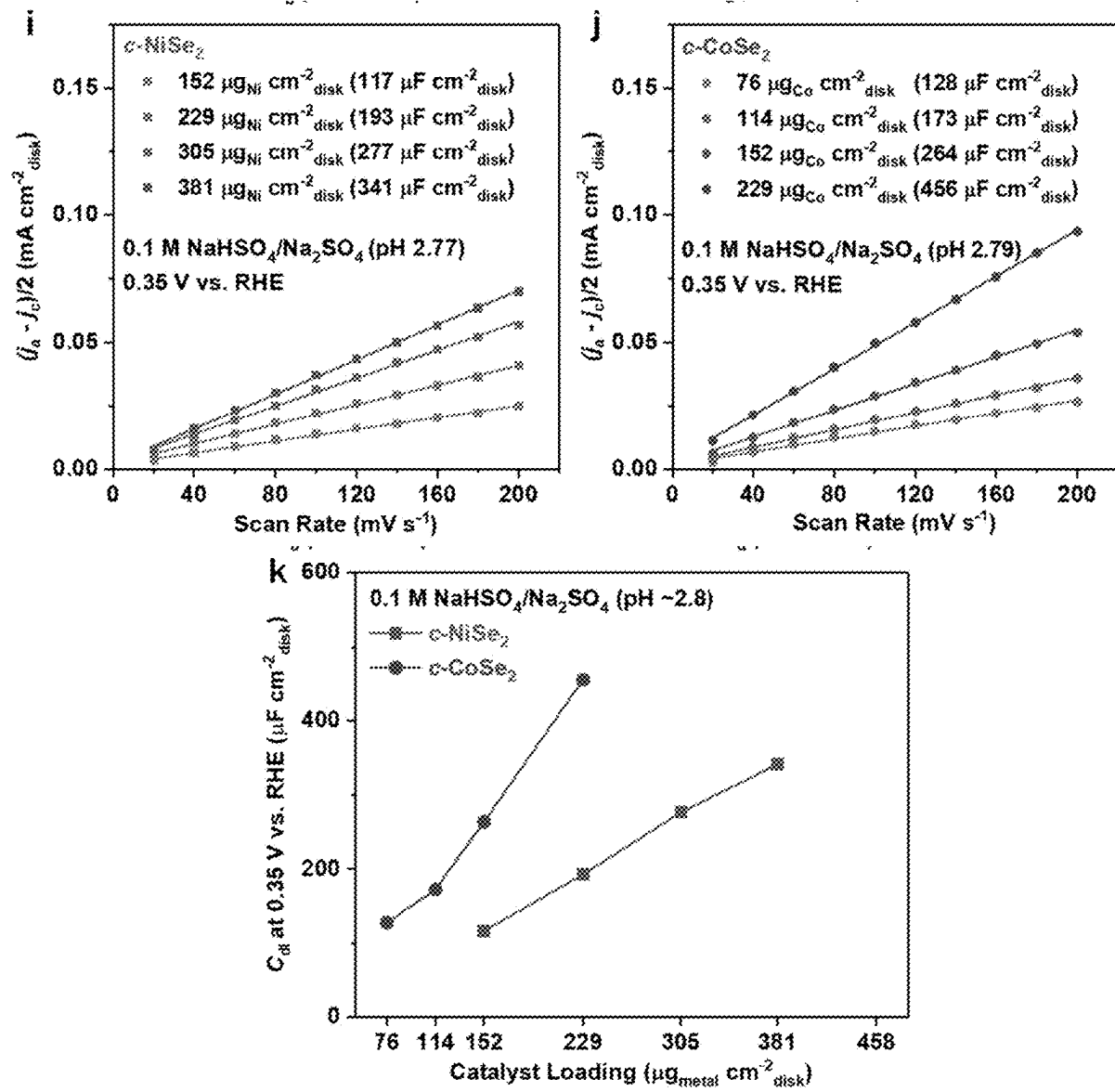


FIG. 11 continued

disk: potentiostatic (0.75 V vs. RHE); ring: potentiodynamic (between 0.05 V and 1.2 V vs. RHE)
 disk: potentiodynamic (from 0.75 V to -0.025 V vs. RHE); ring: potentiostatic (1.3 V vs. RHE)

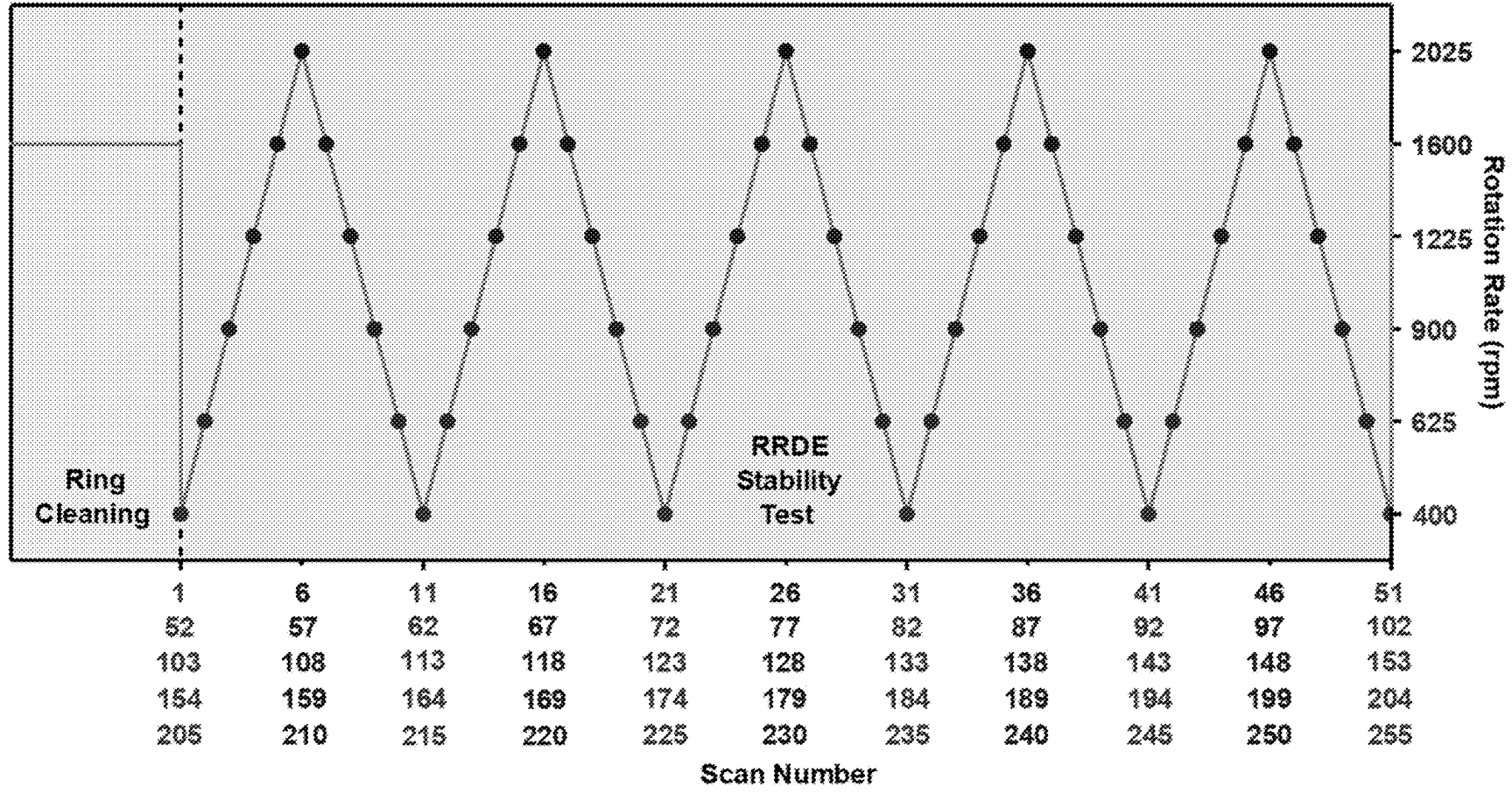


FIG. 12

FIG. 13

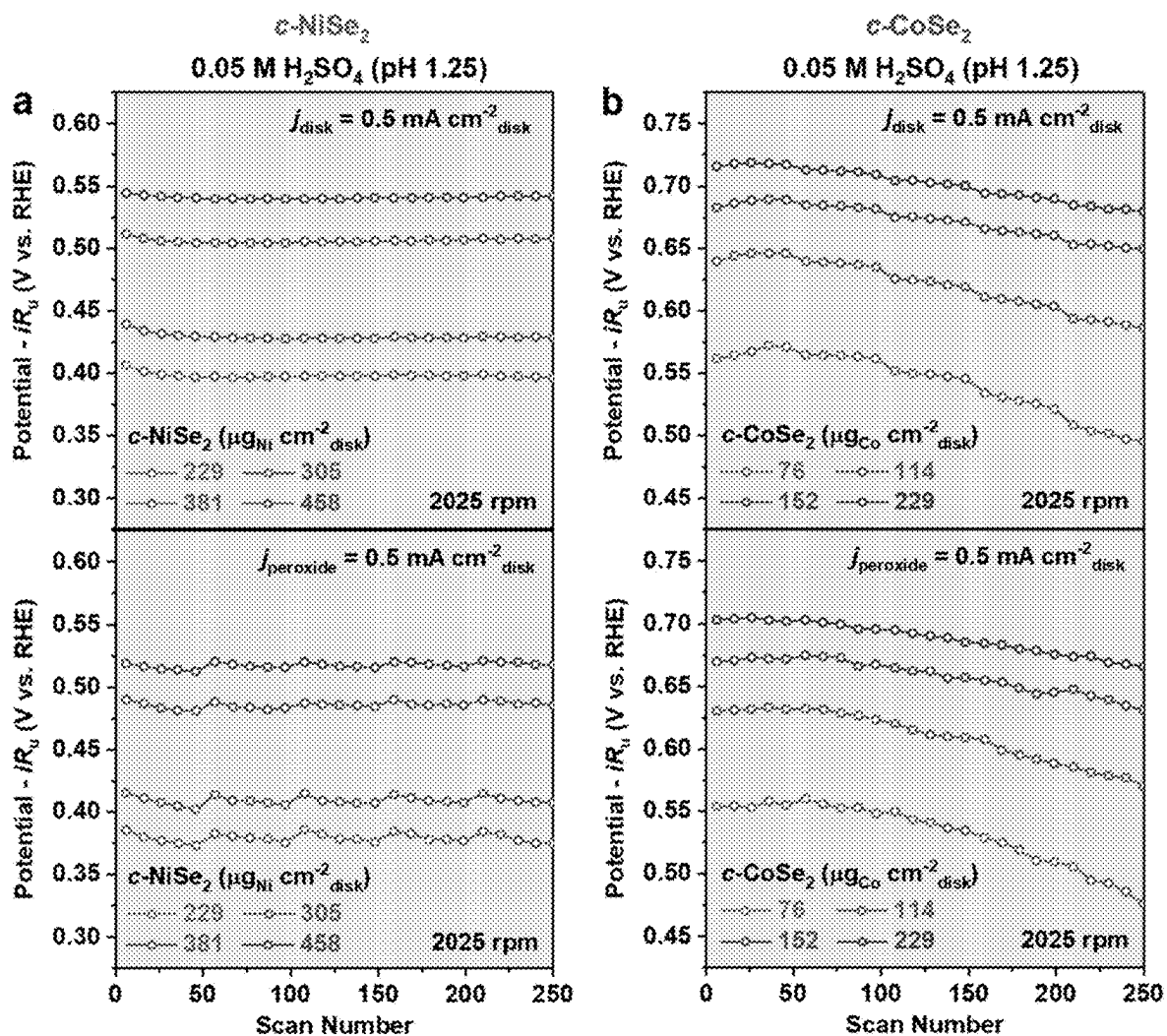


FIG. 14

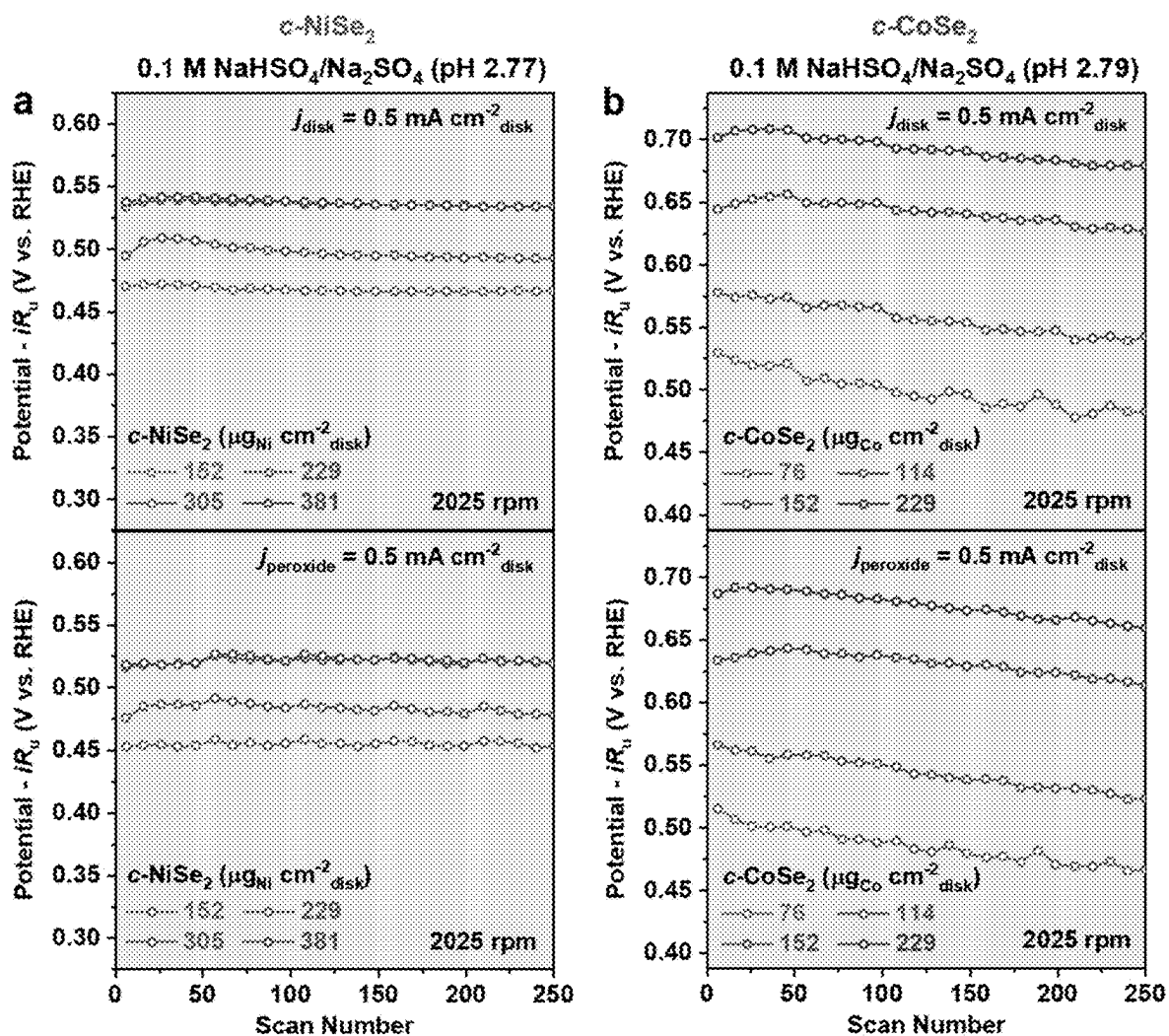


FIG. 15

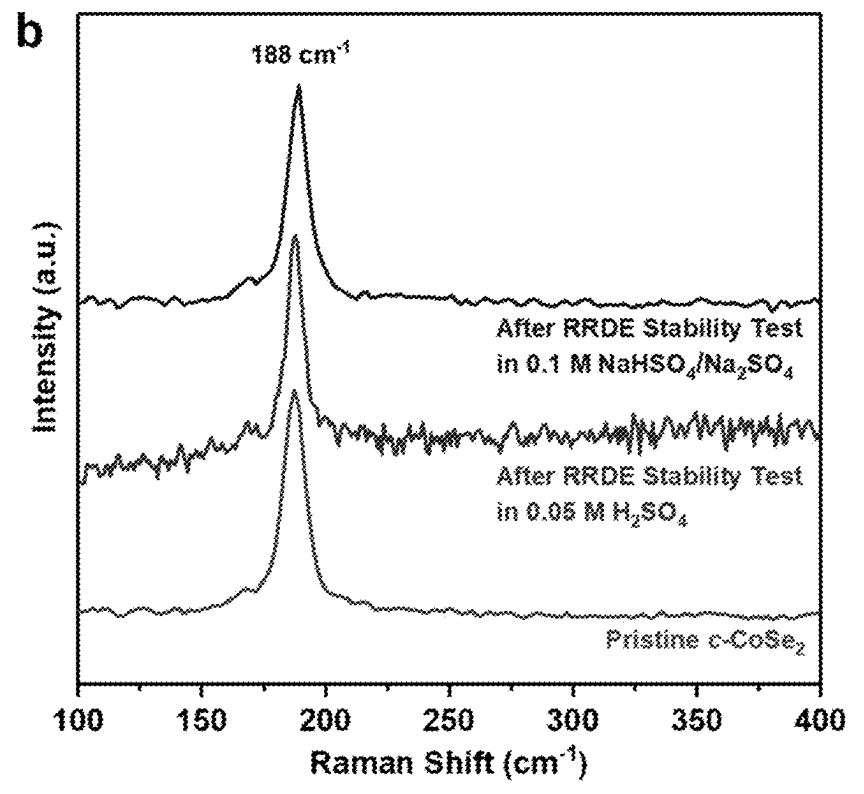
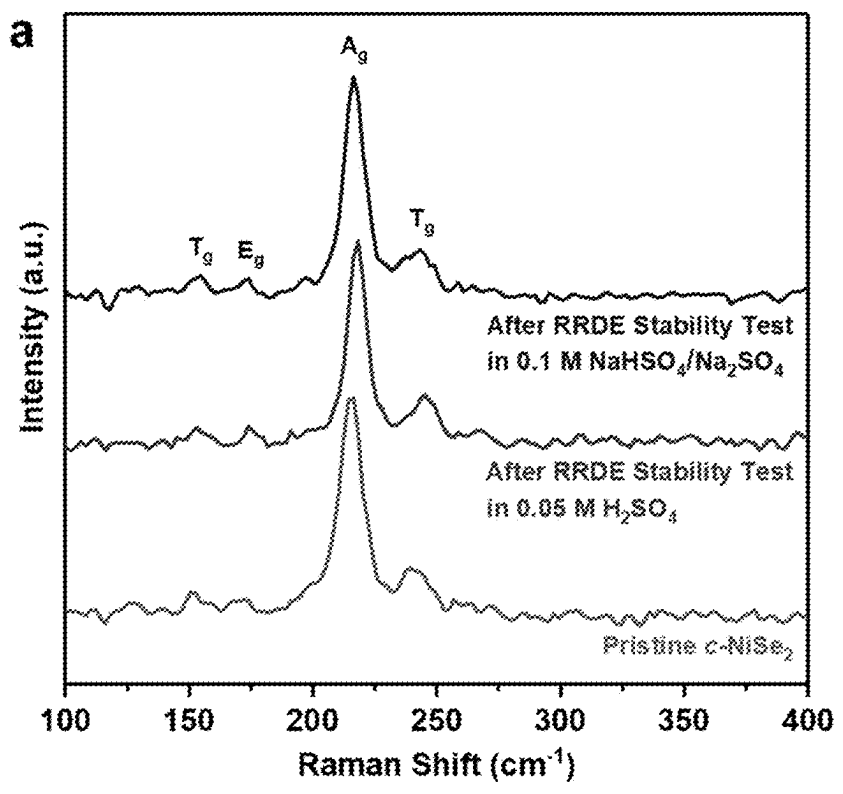


FIG. 15 Continued

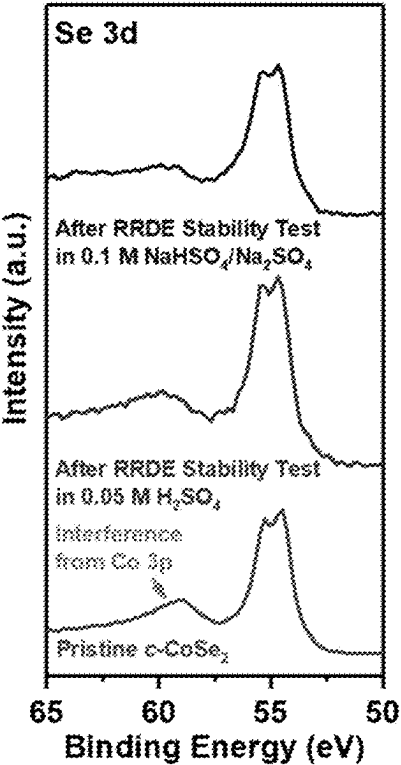
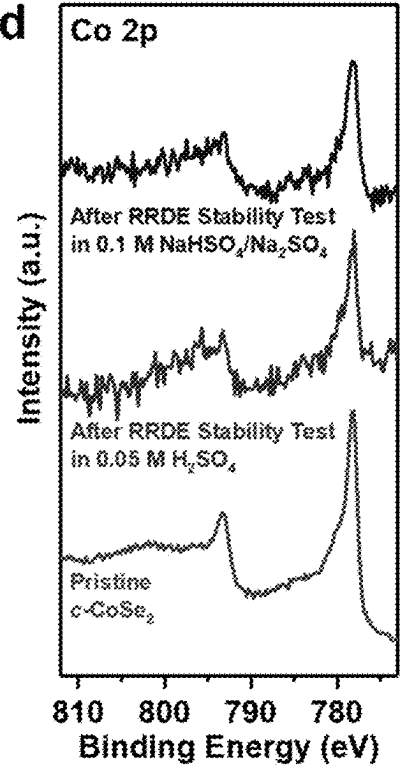
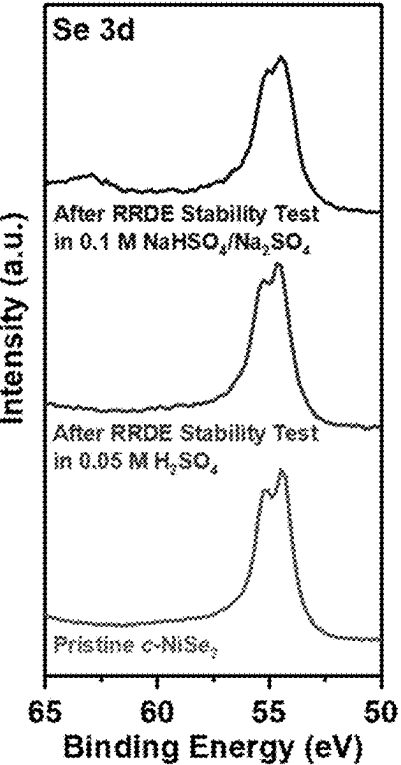
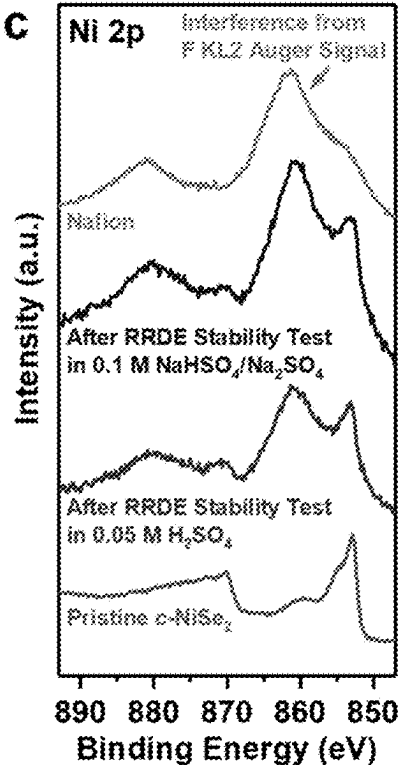


FIG. 16

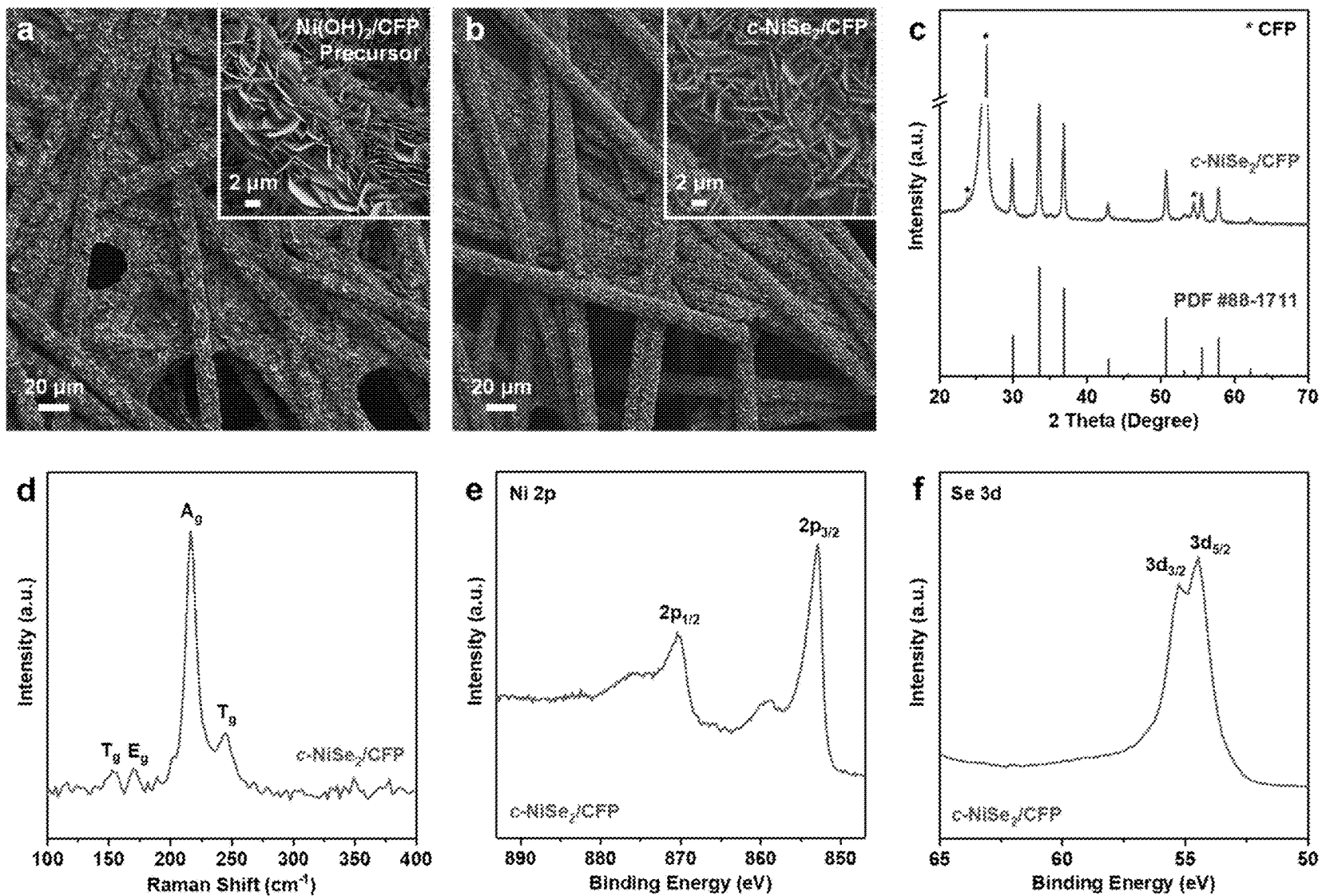
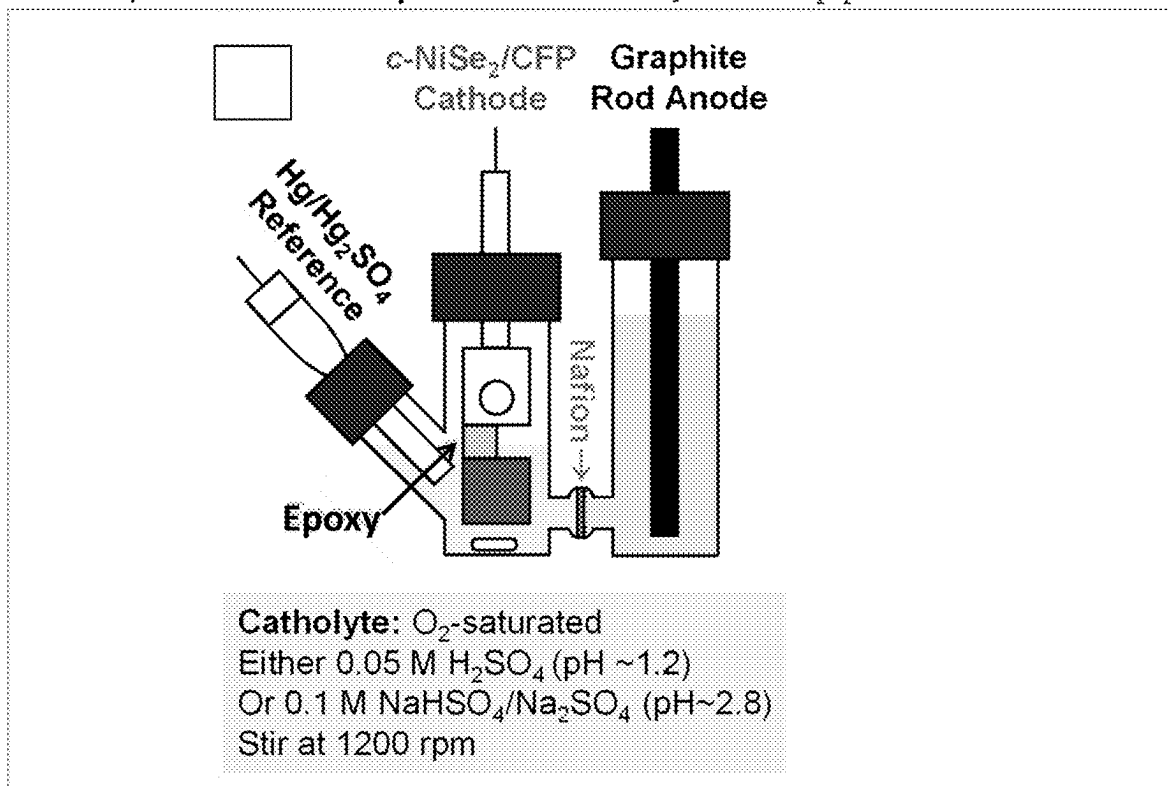


FIG. 17

Two-Compartment Three-Electrode H-Cell for Bulk Electrolysis of H_2O_2 in Acidic Solution



Anolyte:
0.05 M H_2SO_4 (pH ~1.2)

c-NiSe₂/CFP Cathode:
0.60 V vs. RHE

FIG. 18

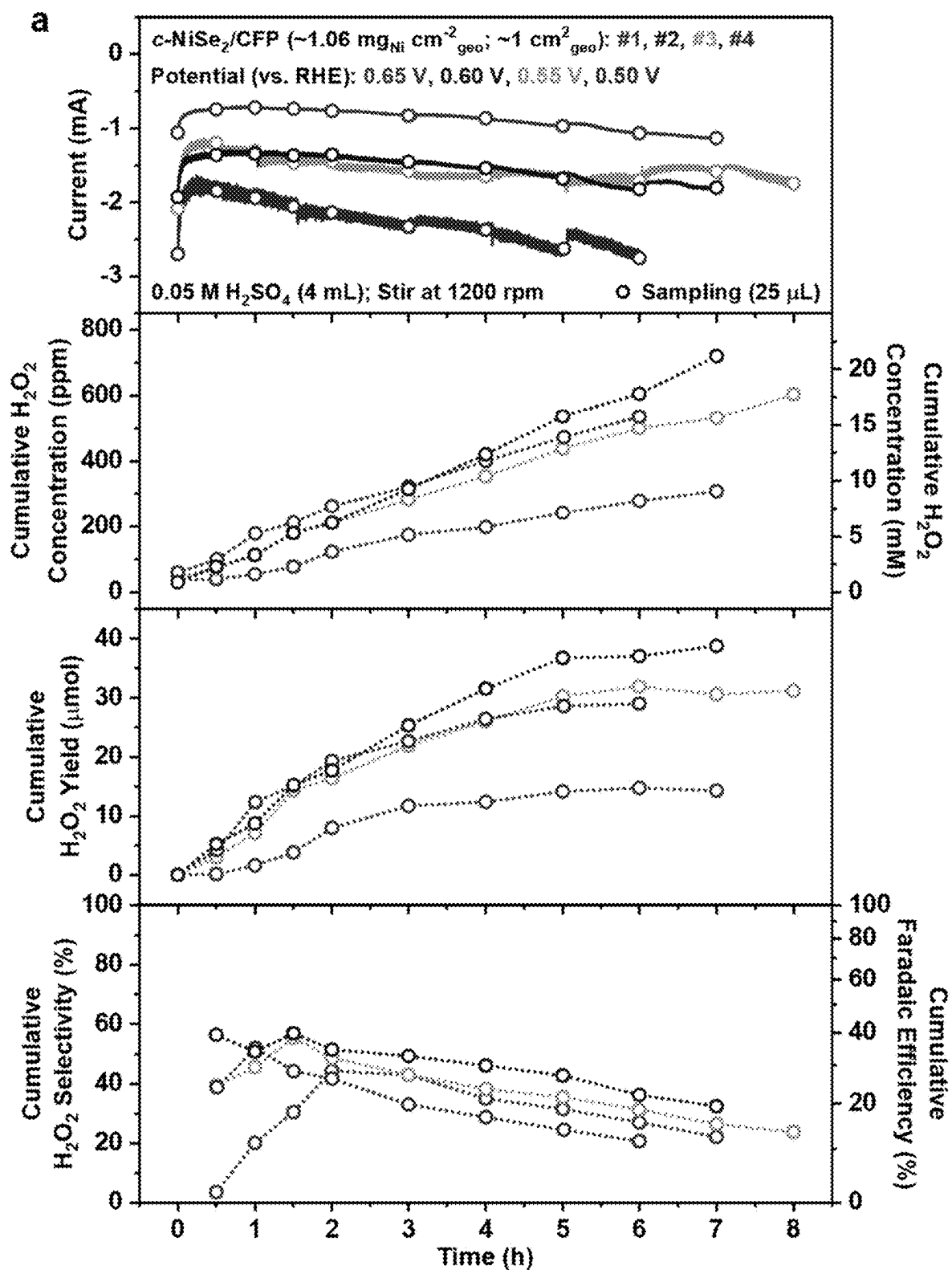


FIG. 18 Continued

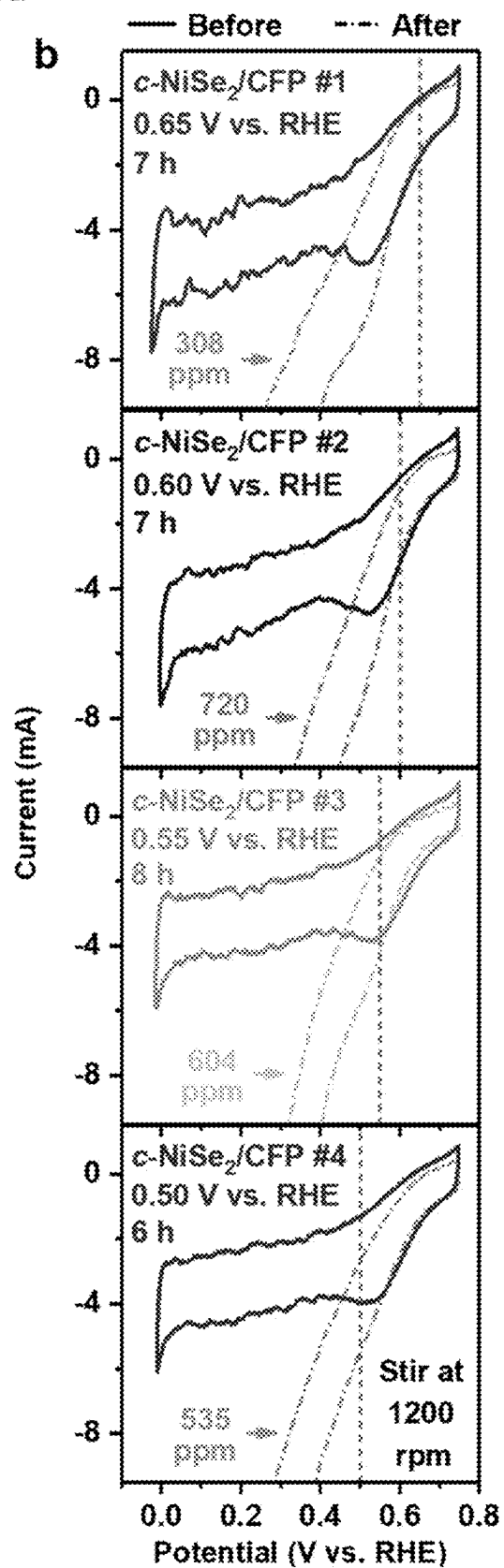


FIG. 19

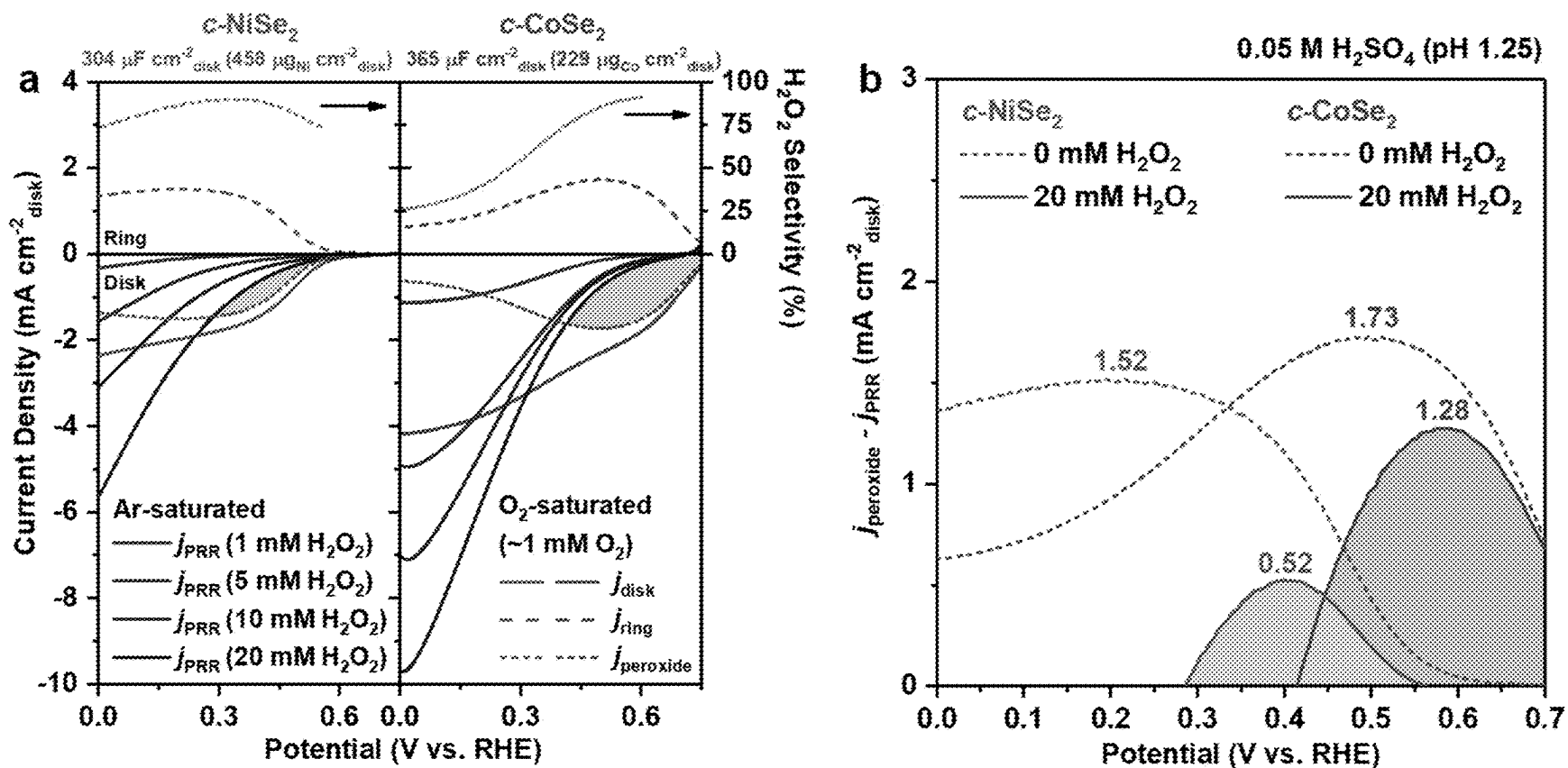


FIG. 20

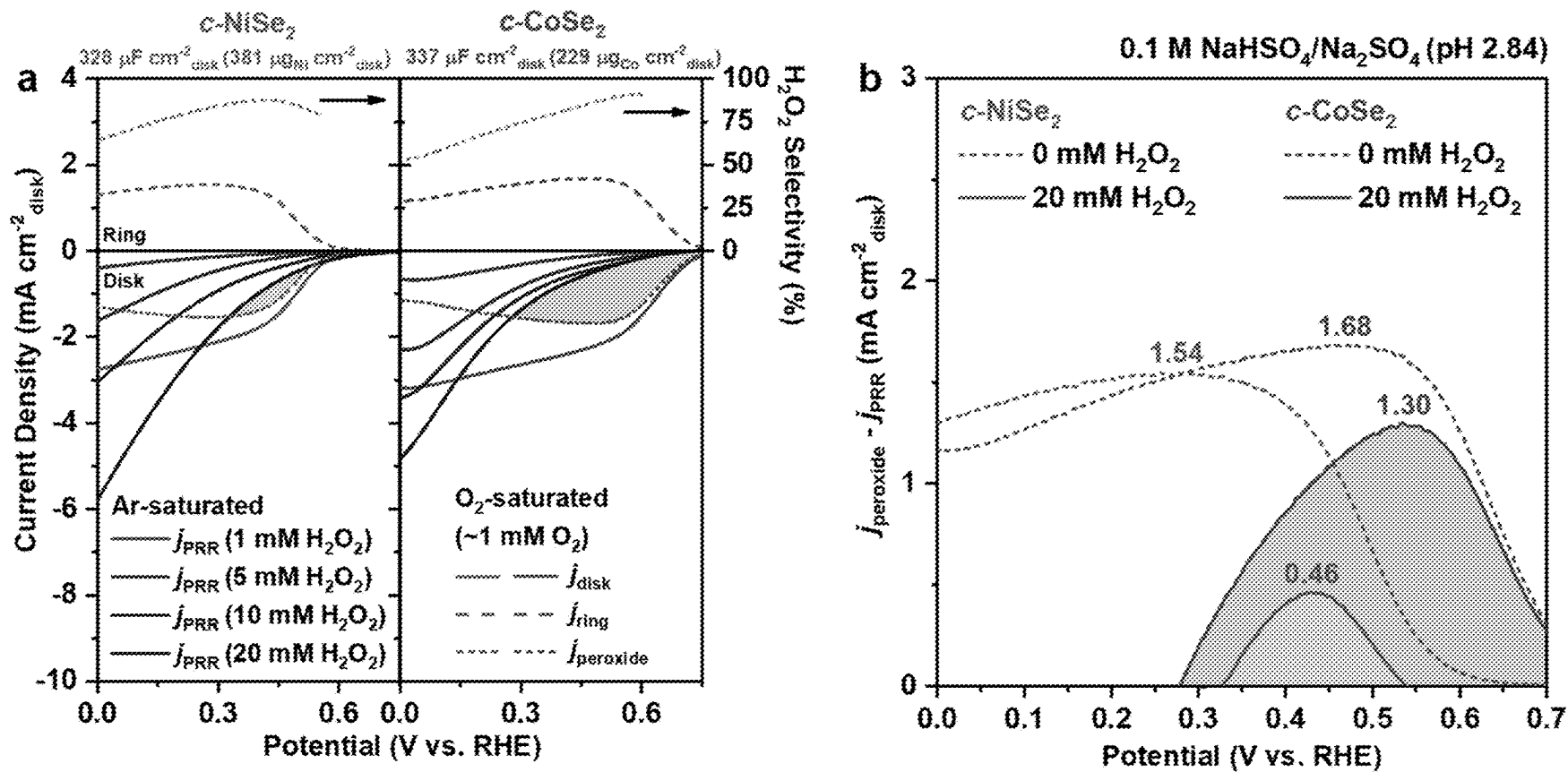


FIG. 21

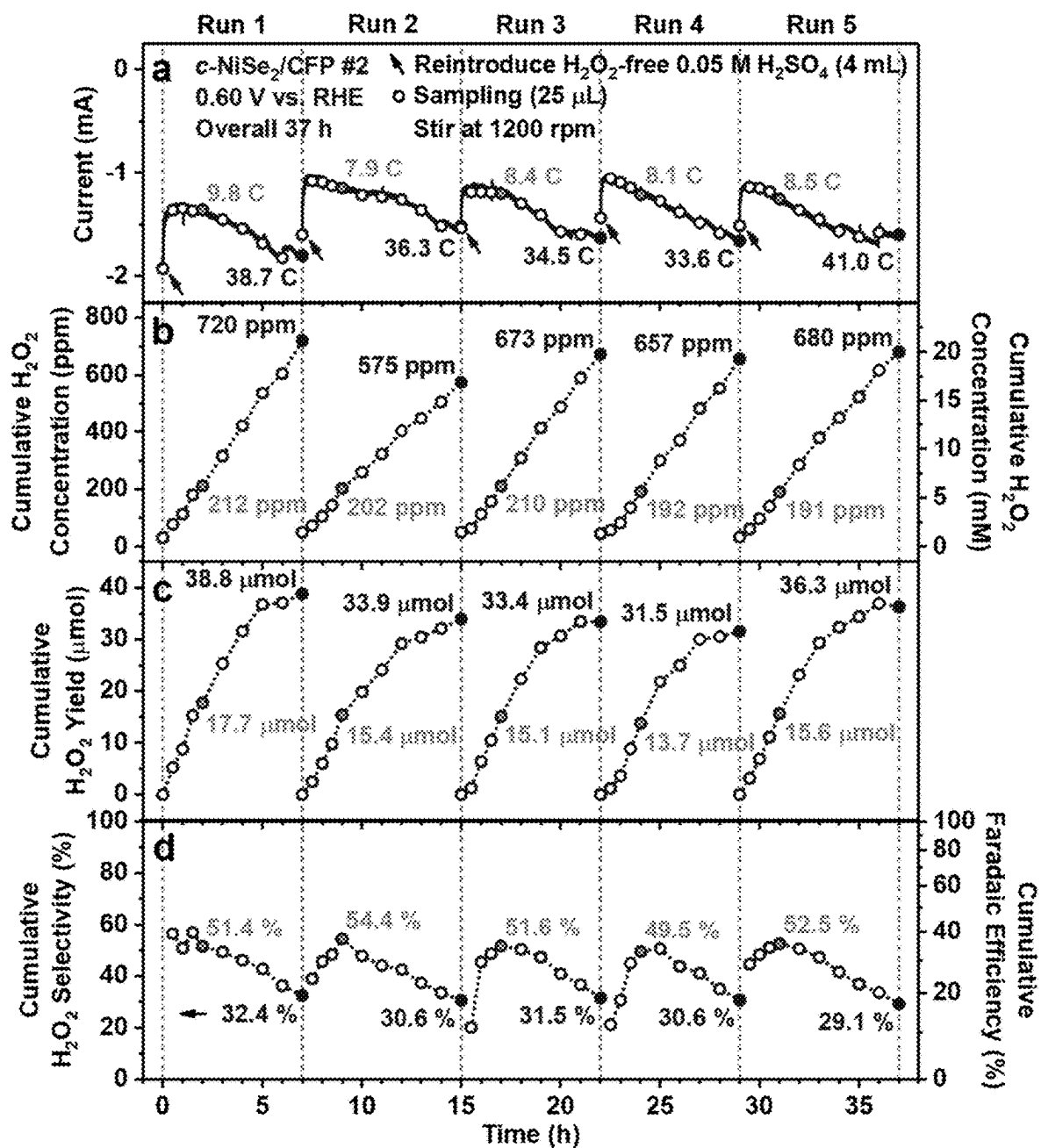


FIG. 22

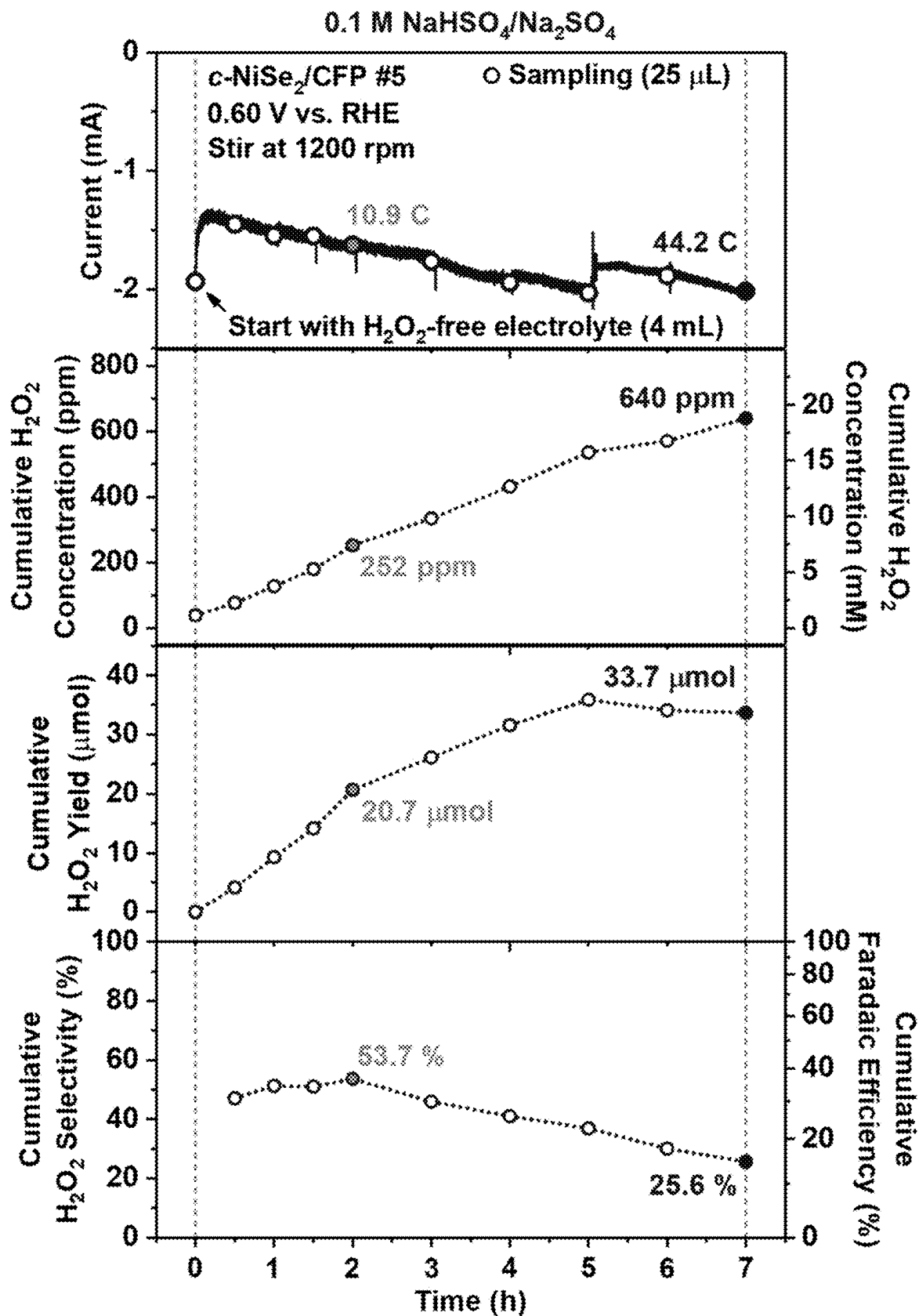


FIG. 23

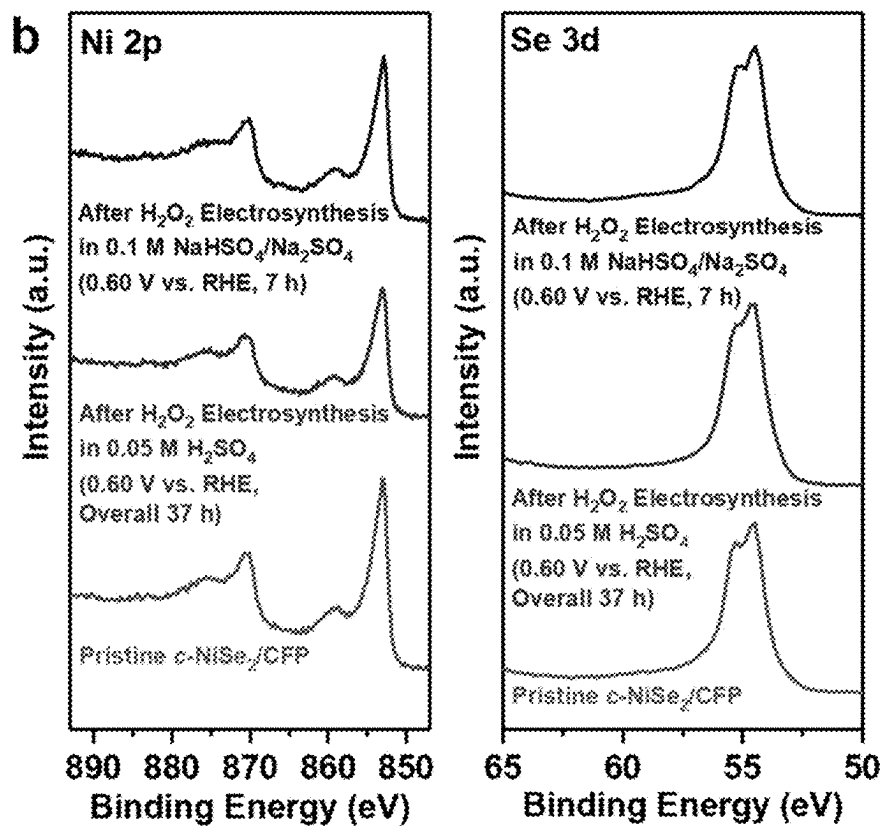
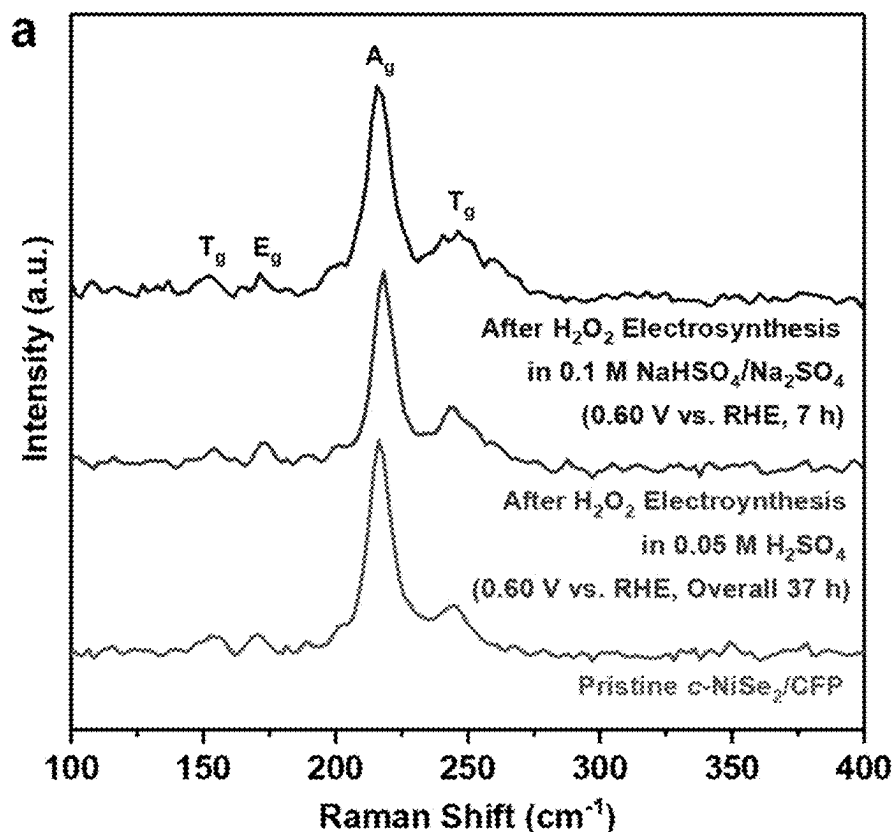


FIG. 23 continued

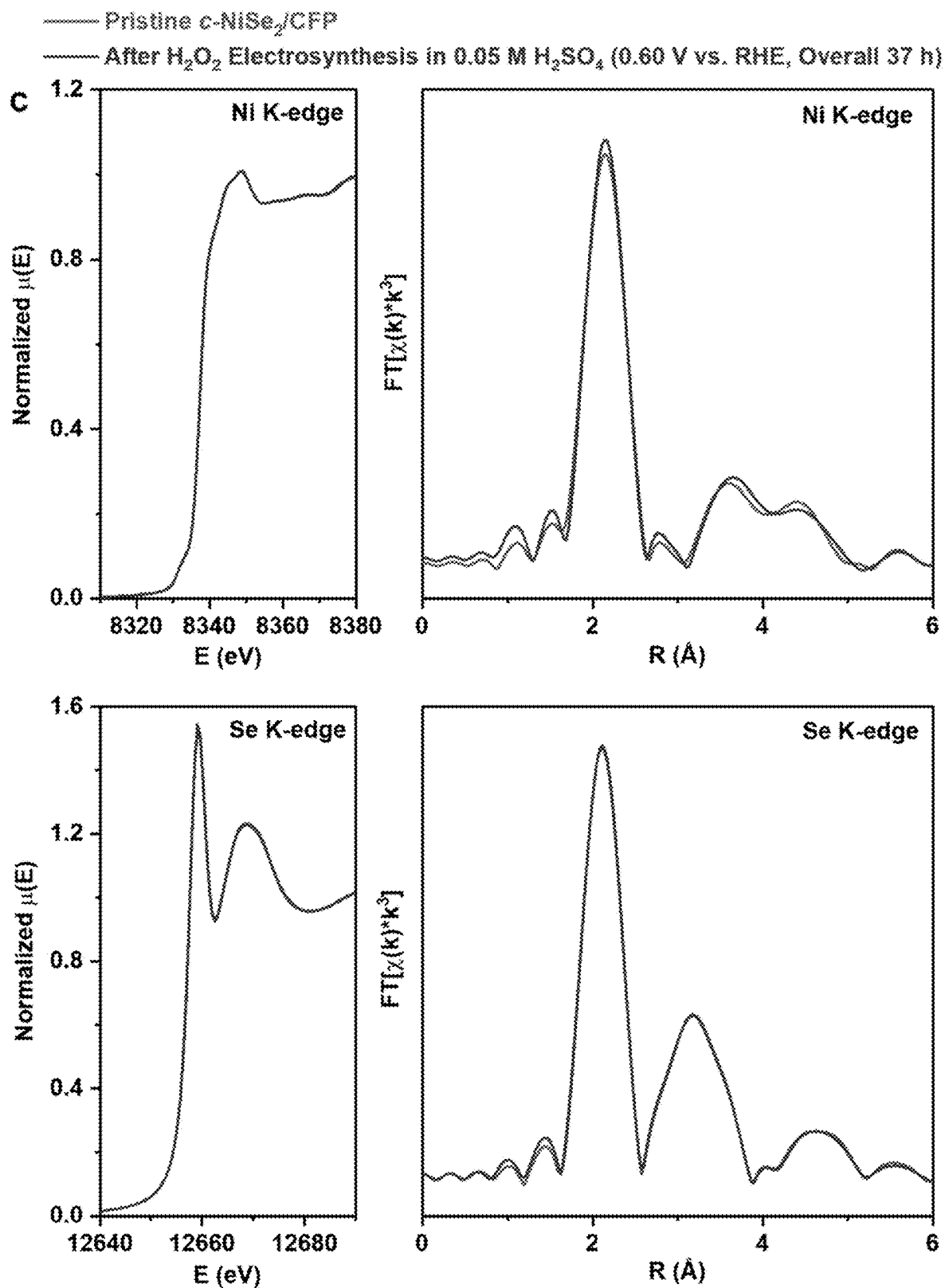


FIG. 23 continued

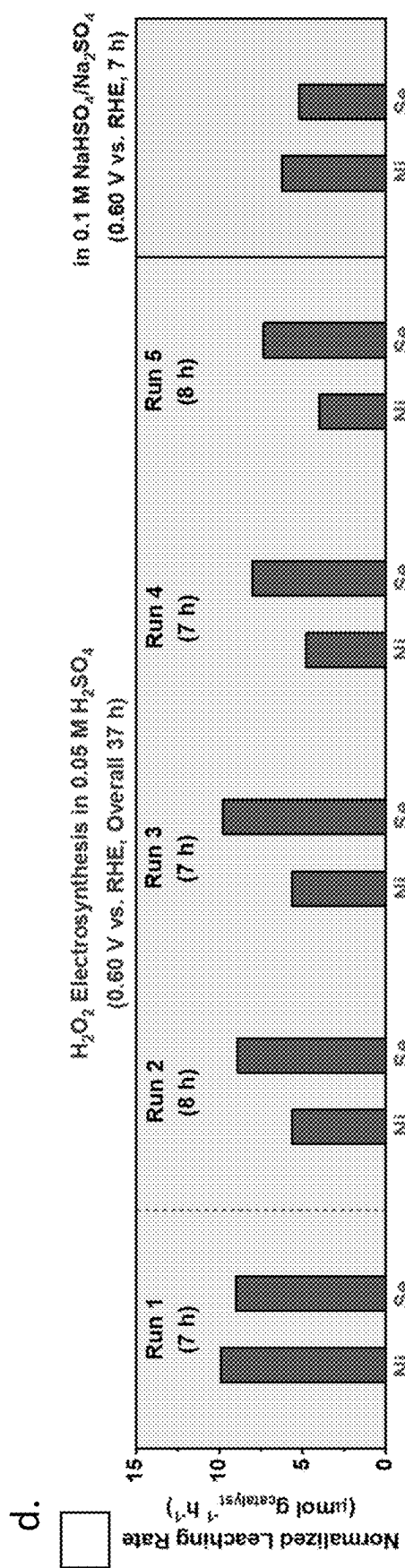


FIG. 24

Half-Cell Studies of the Electro-Fenton Process for Glycerol Valorization at $c\text{-NiSe}_2$ Cathode

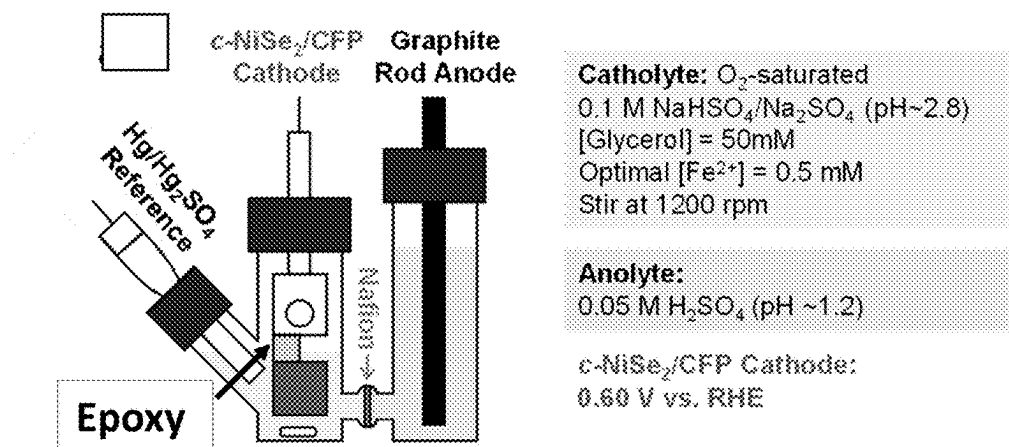


FIG. 25

Half-Cell Studies of the Electro-Fenton Process for Glycerol Valorization at c-NiSe₂ Cathode ([Fe²⁺] = 0.5 mM)

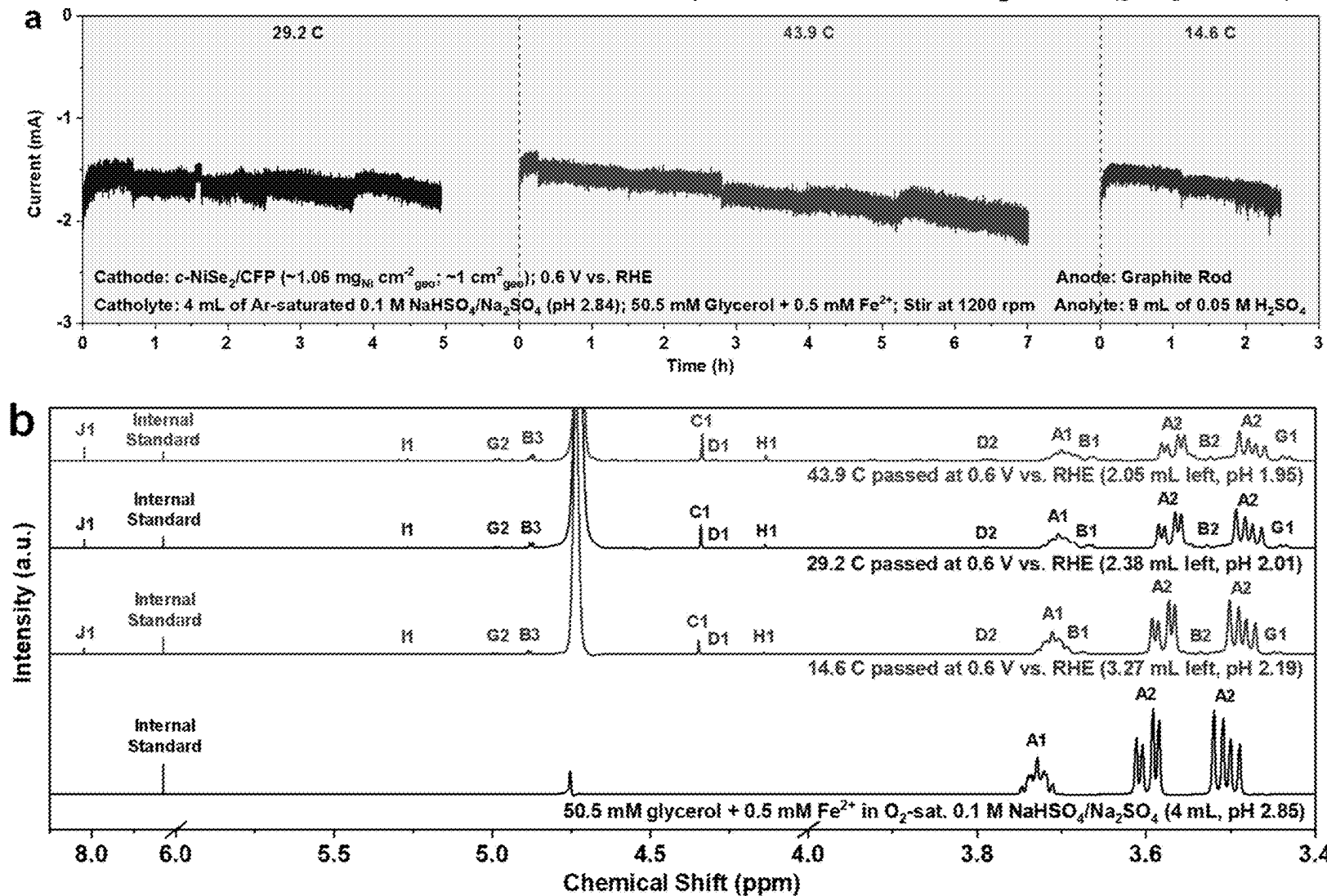


FIG. 27

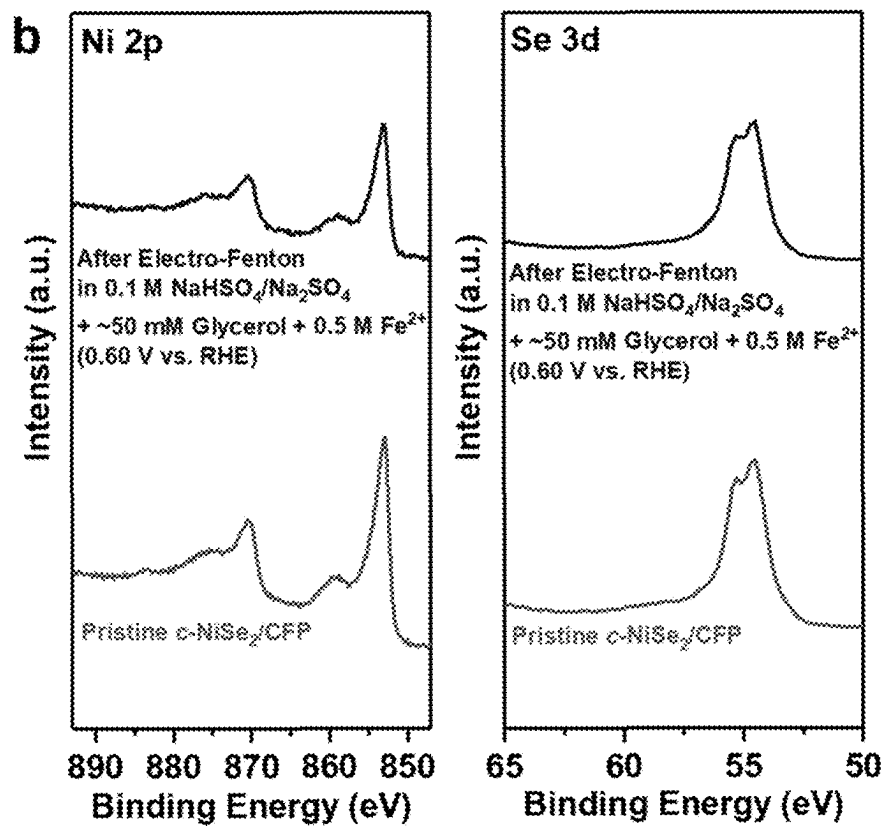
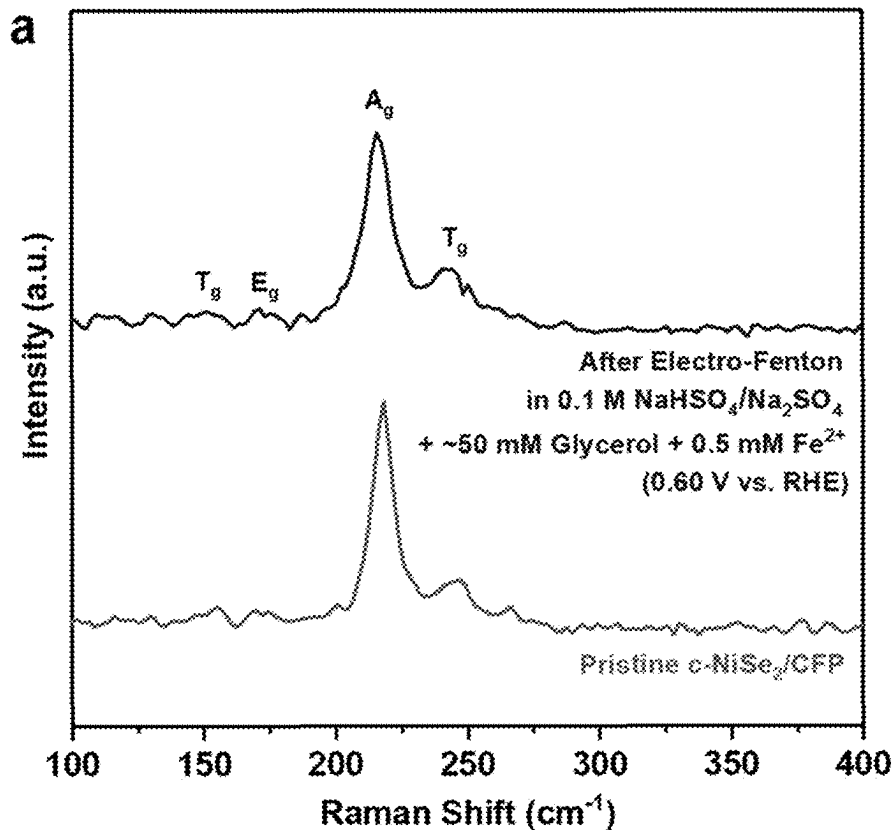


FIG. 28

Half-Cell Studies of Direct Anodic Oxidation of Glycerol at Pt/C Anode

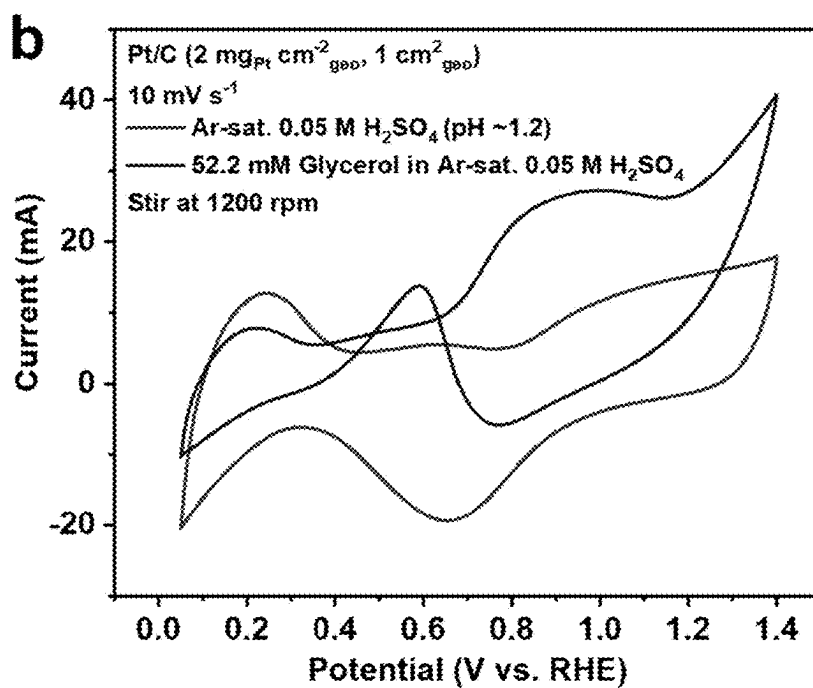
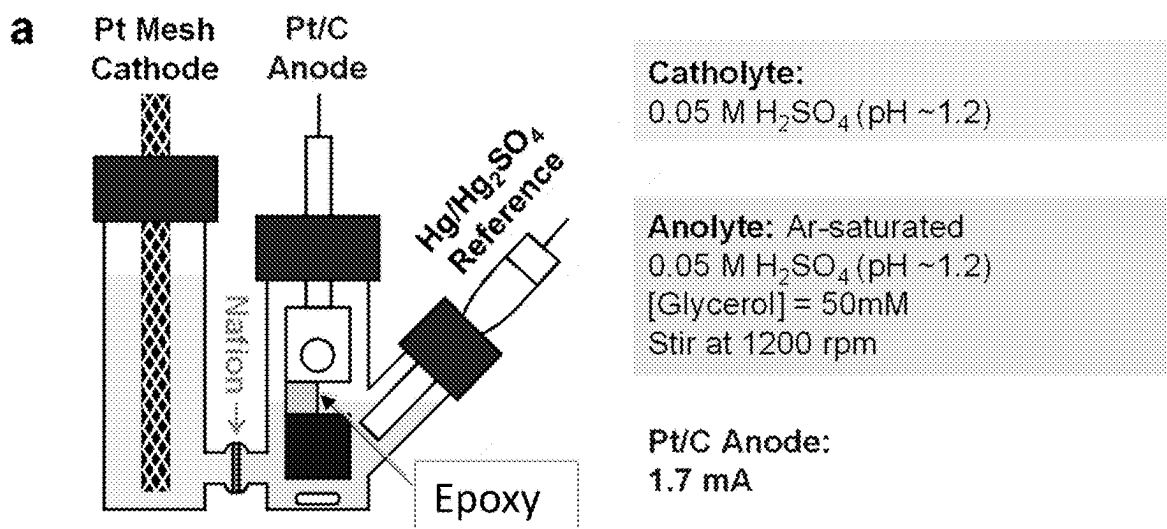


FIG. 28 continued

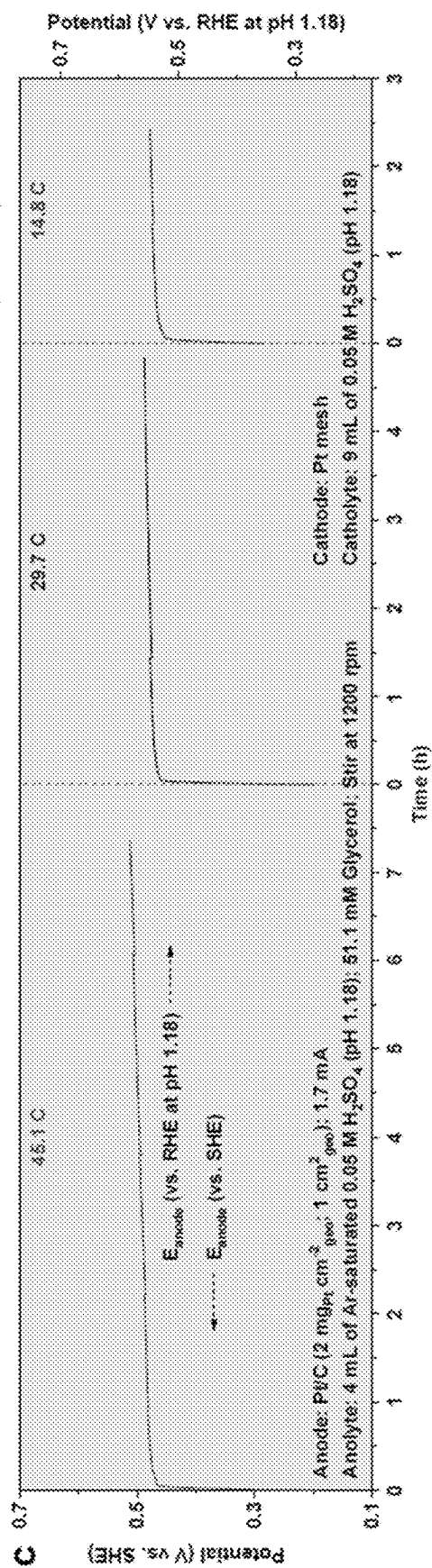


FIG. 28 continued

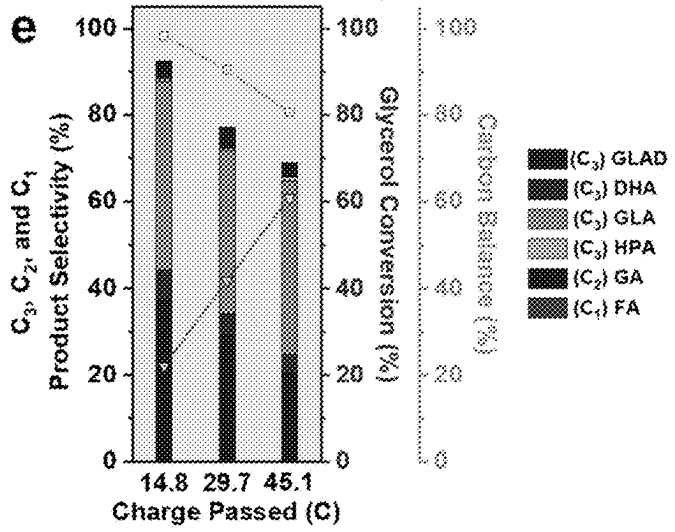
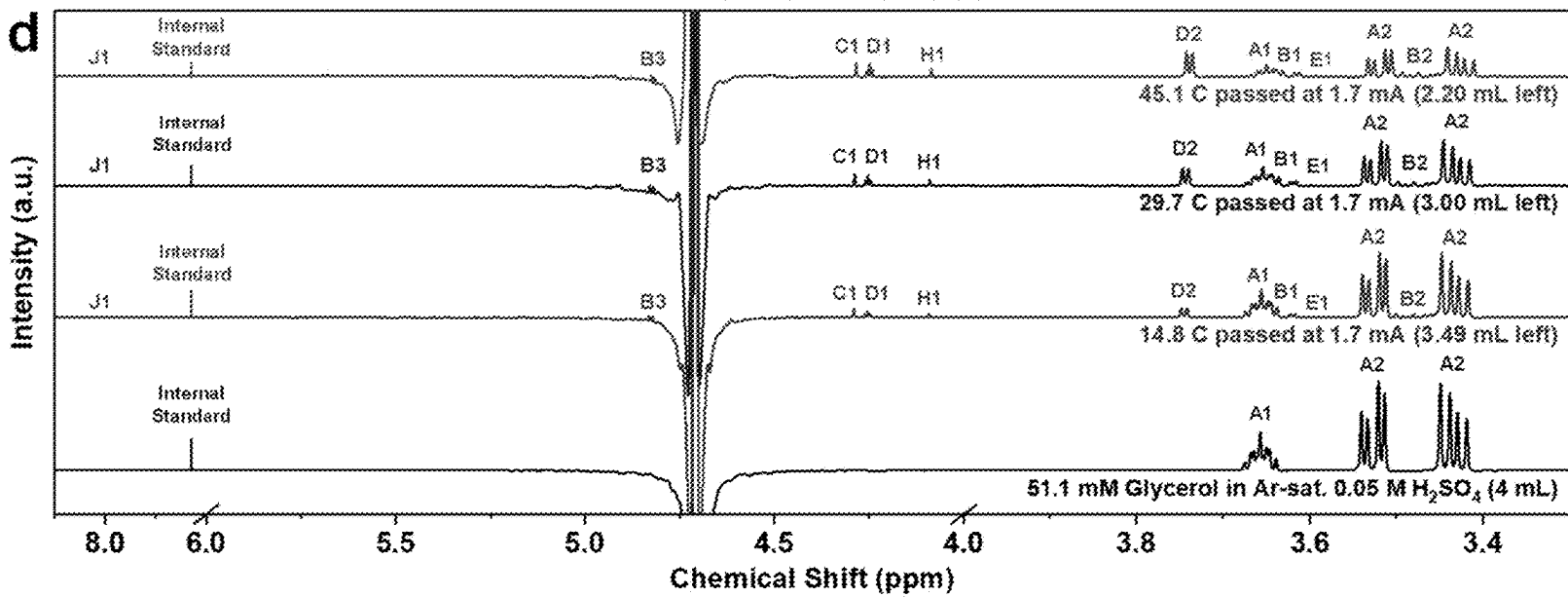
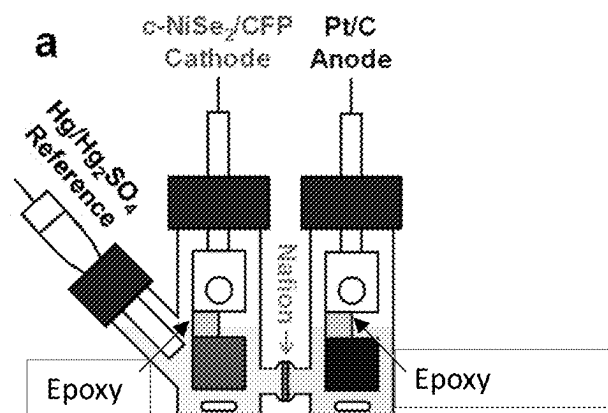


FIG. 29

Two-Compartment Three-Electrode H-Cell for Linear Paired Electrochemical Valorization of Glycerol at *c*-NiSe₂ Cathode and Pt/C Anode



Catholyte: O₂-saturated
0.1 M or 0.5 M NaHSO₄/Na₂SO₄ (pH~2.8)
[Glycerol] = 50mM
Optimum [Fe²⁺] = 0.5 mM
Stir at 1200 rpm

Anolyte: Ar-saturated
0.05 M or 0.5 M H₂SO₄
[Glycerol] = 50 mM
Stir at 1200 rpm

***c*-NiSe₂/CFP Cathode:**
0.60 V vs. RHE (Chronoamperometry)

Pt/C Anode:
Current Match (Chronopotentiometry)

FIG. 30

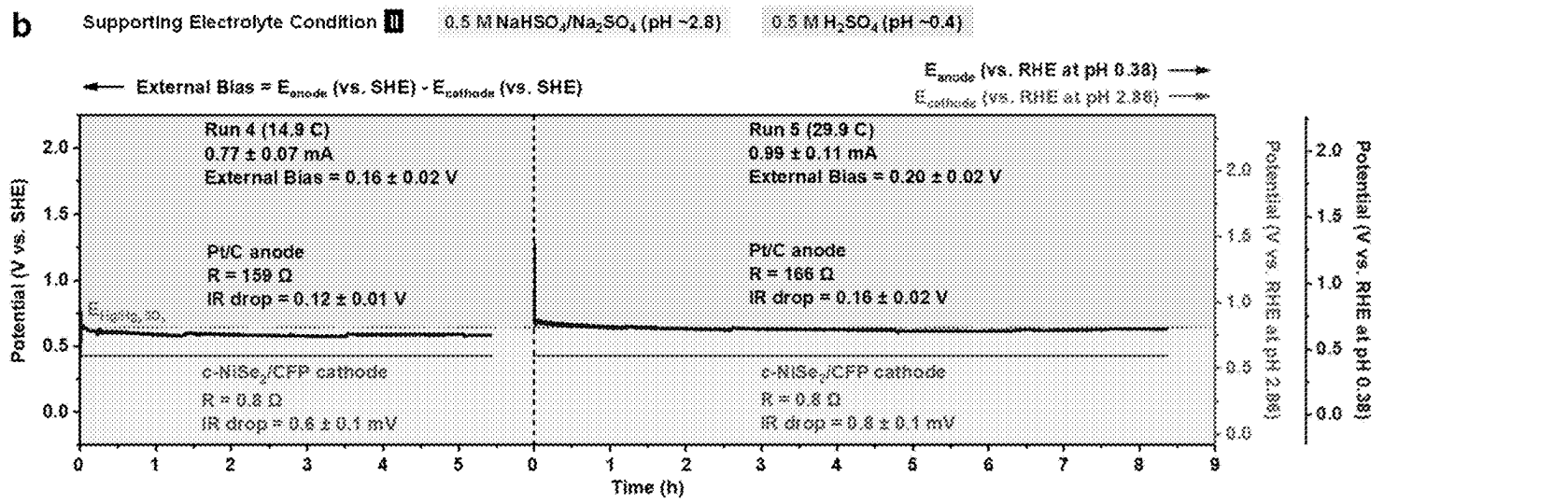
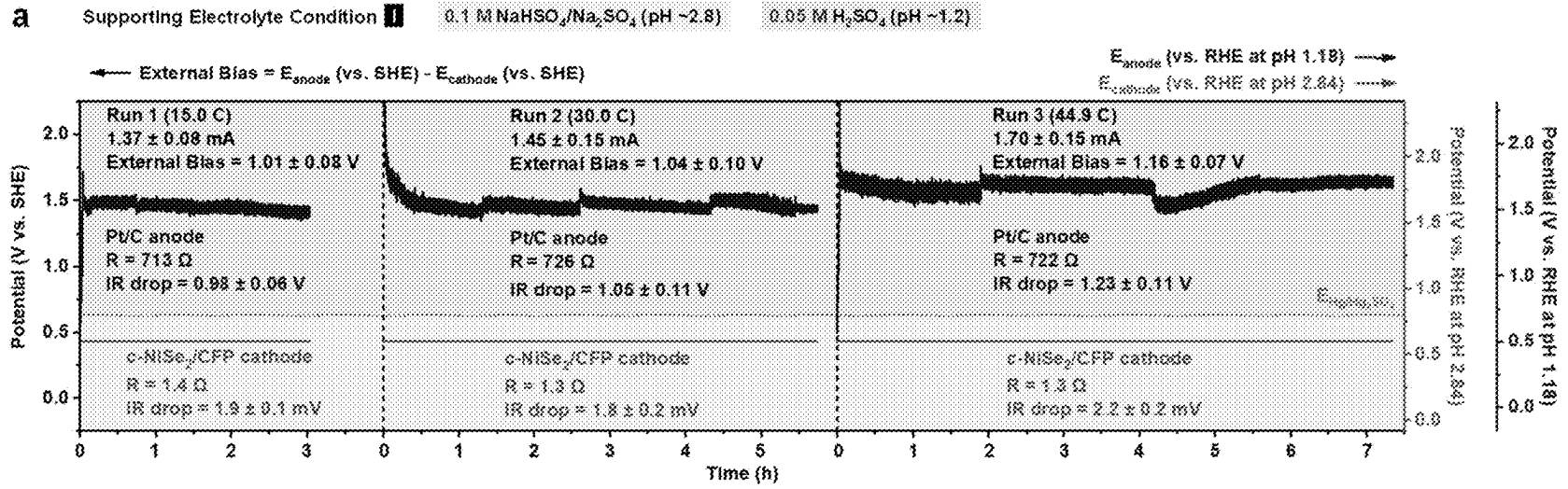


FIG. 31

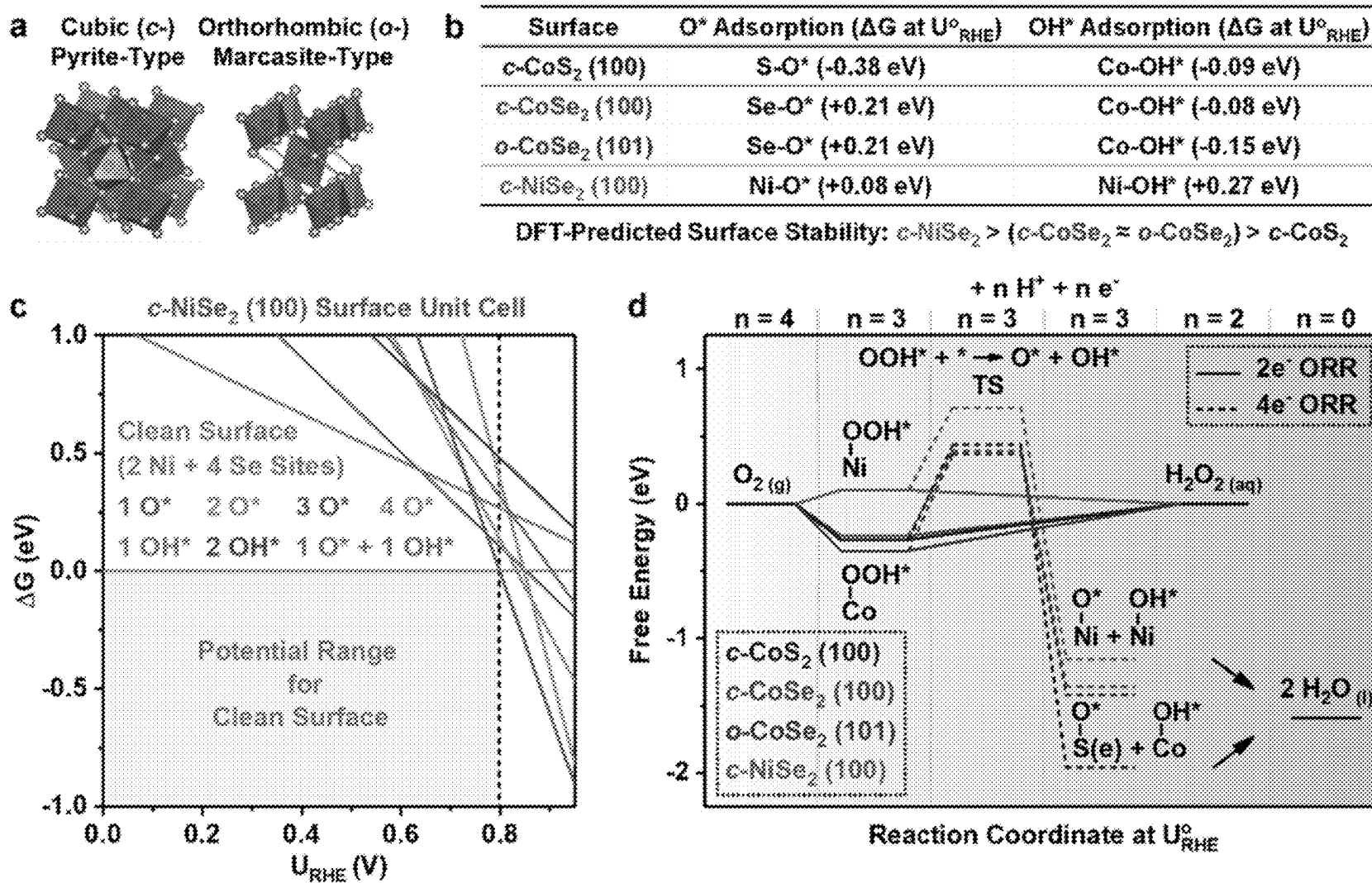


FIG. 32

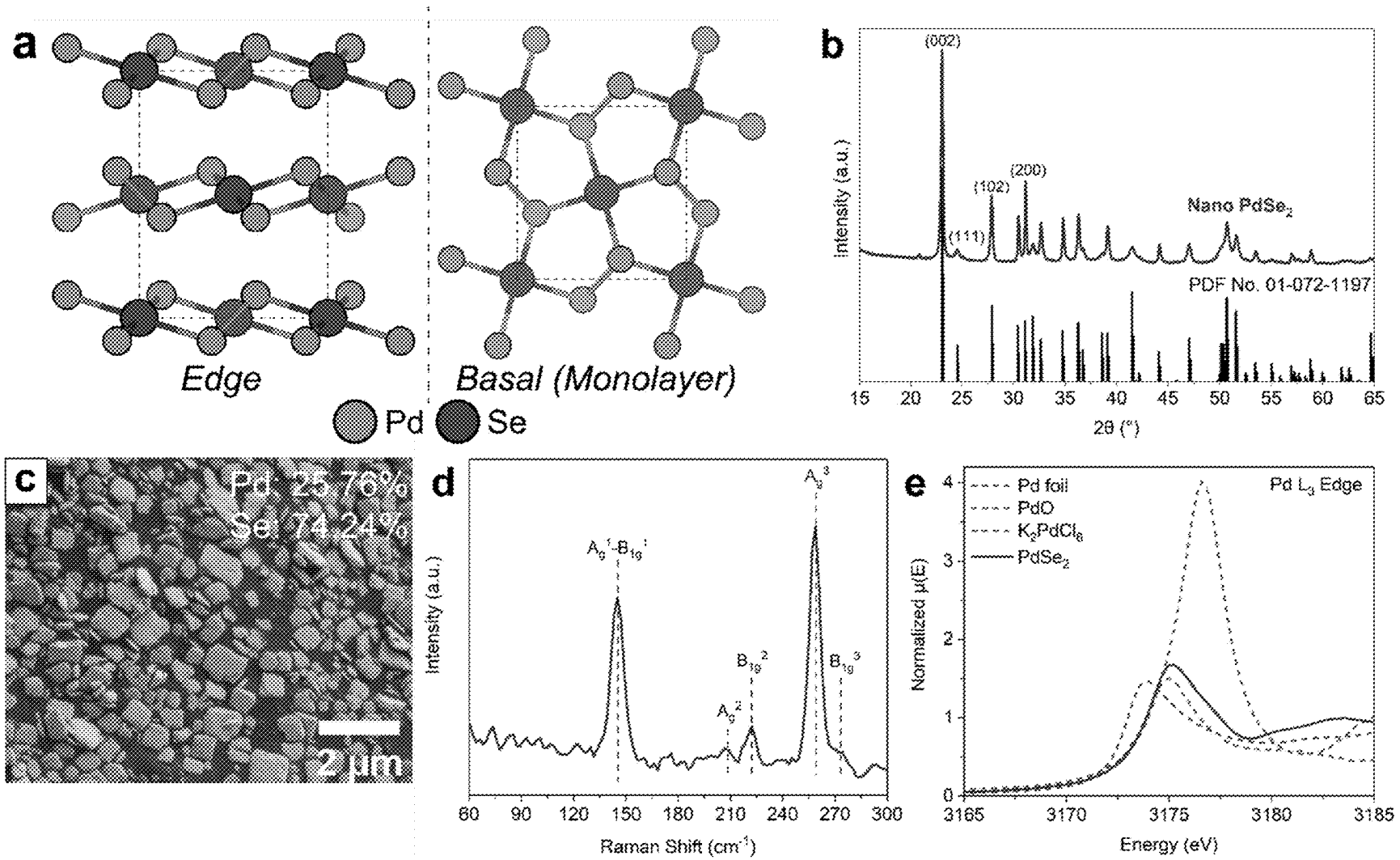


FIG. 33

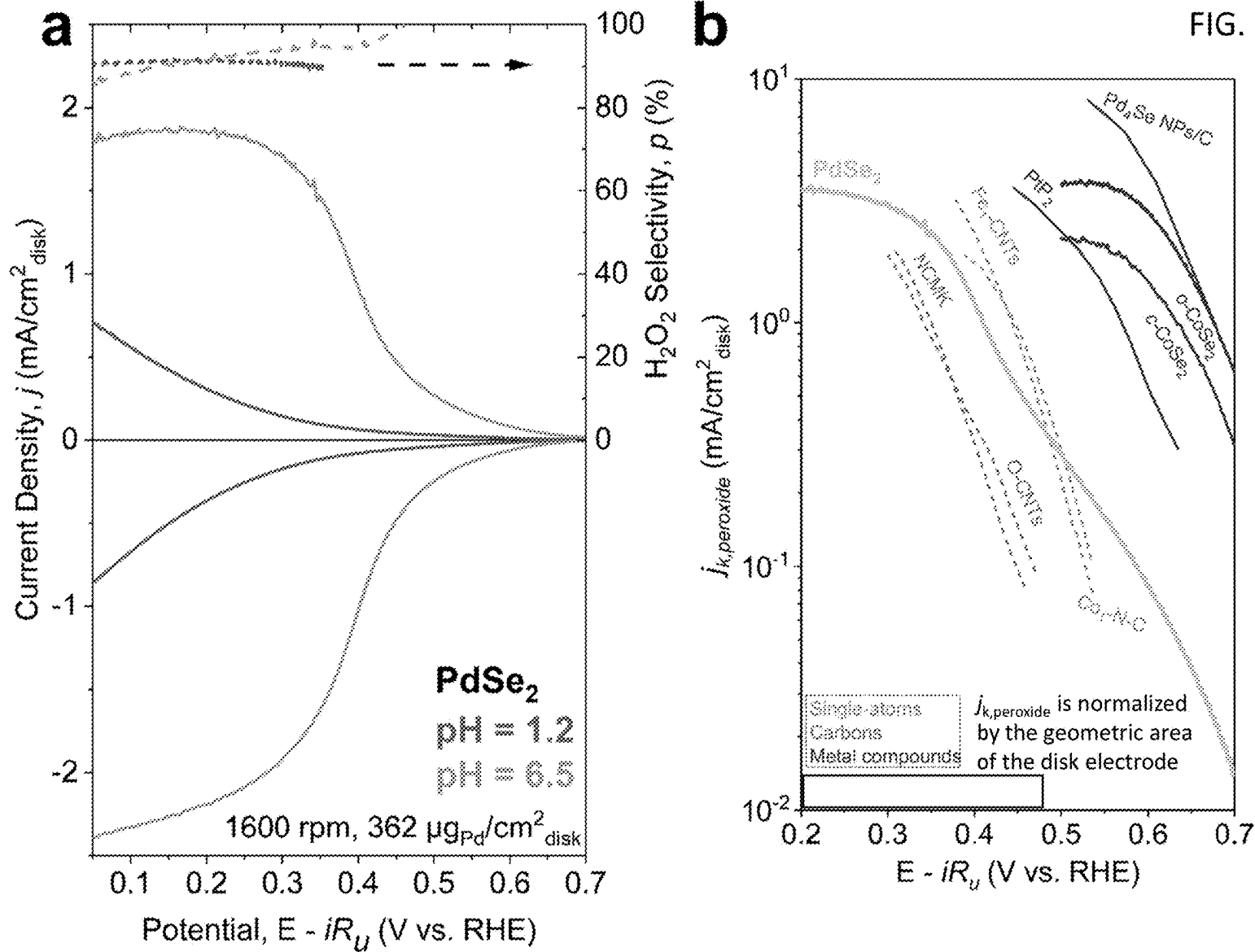


FIG. 33 continued

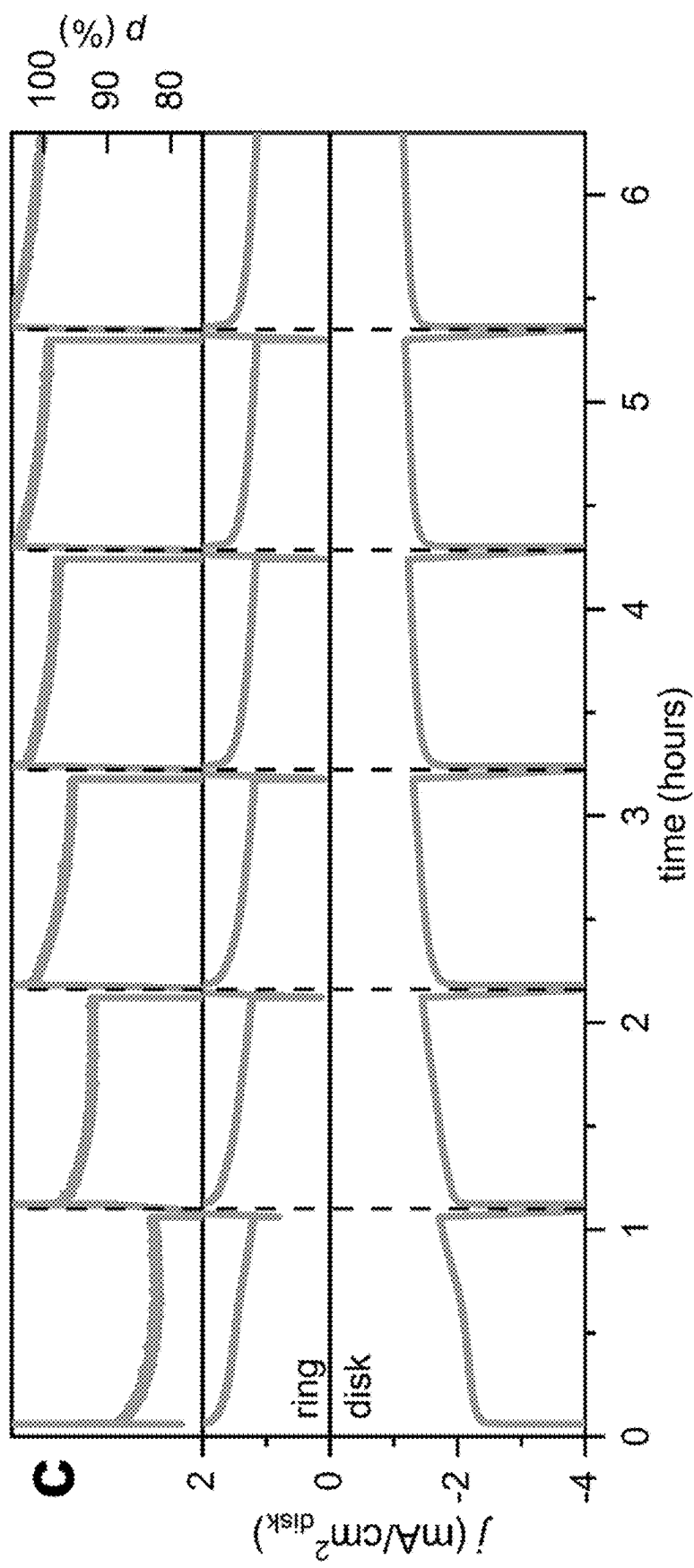


FIG. 34

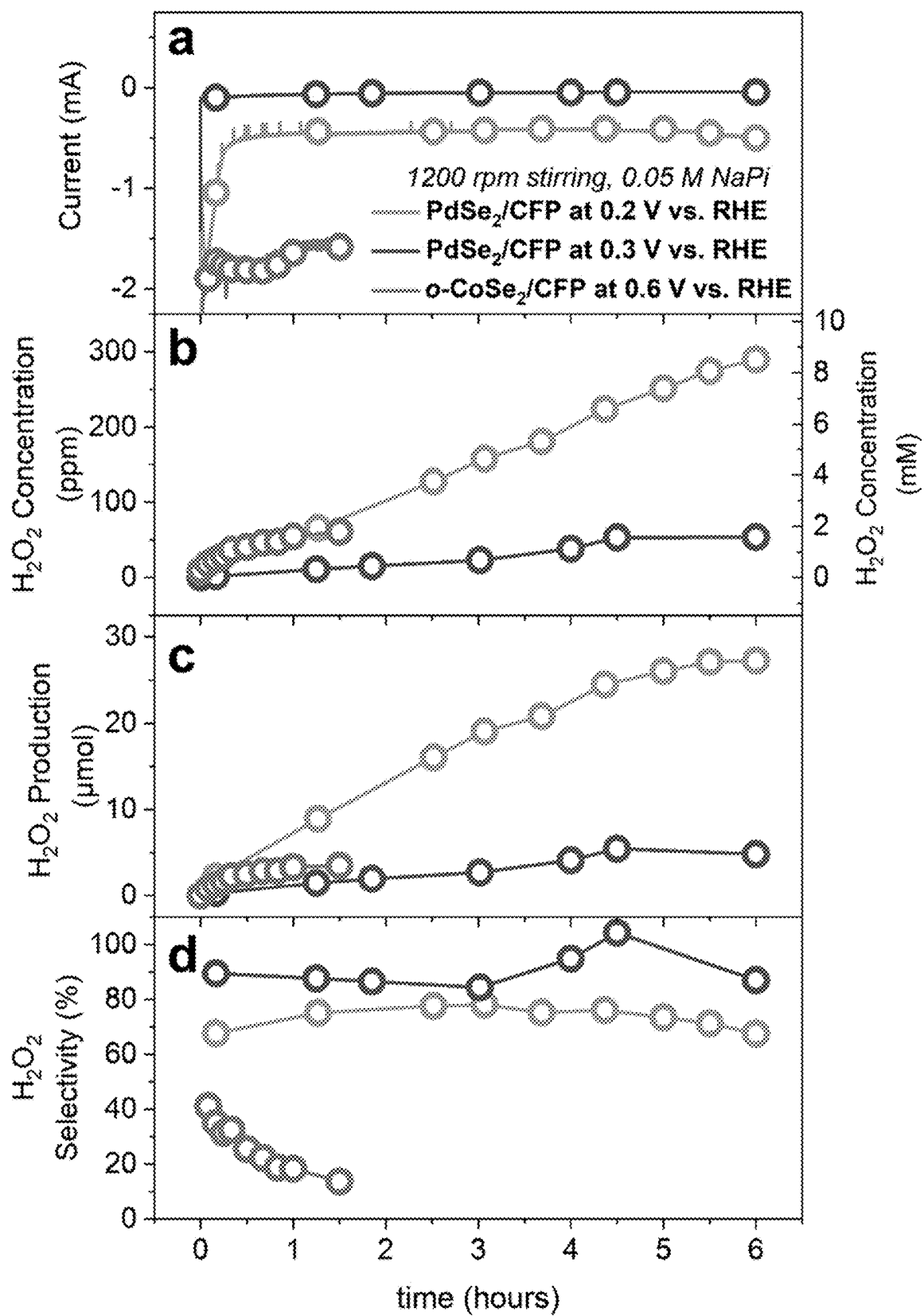


FIG. 35

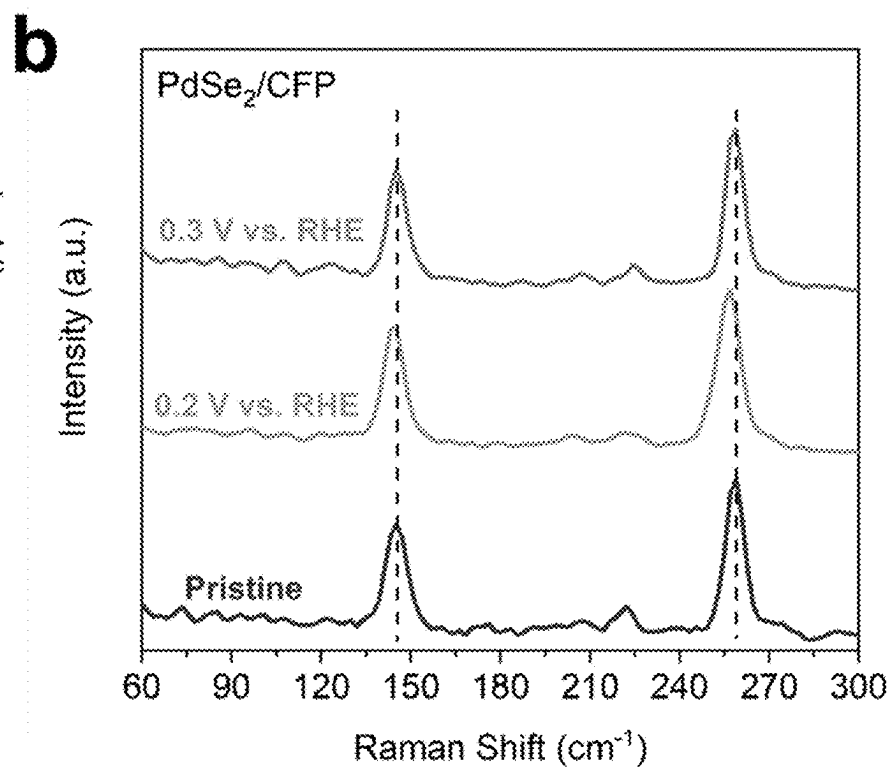
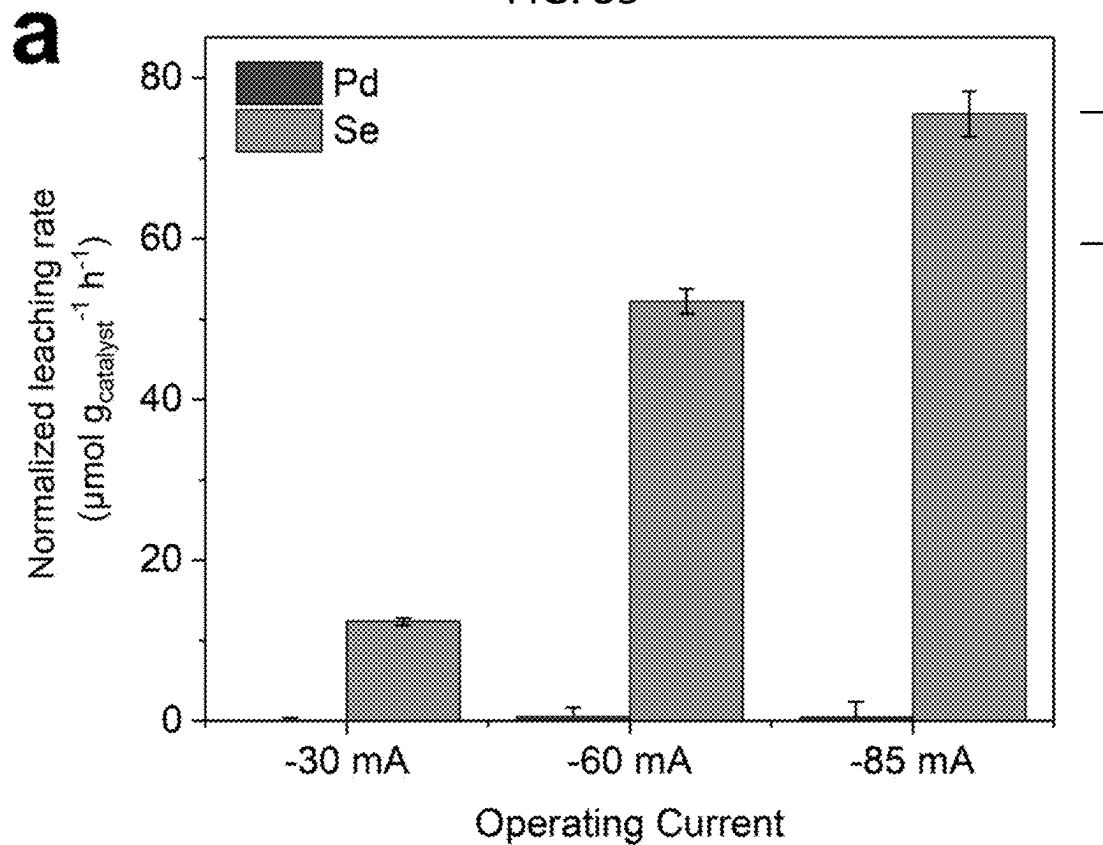


FIG. 35 Continued

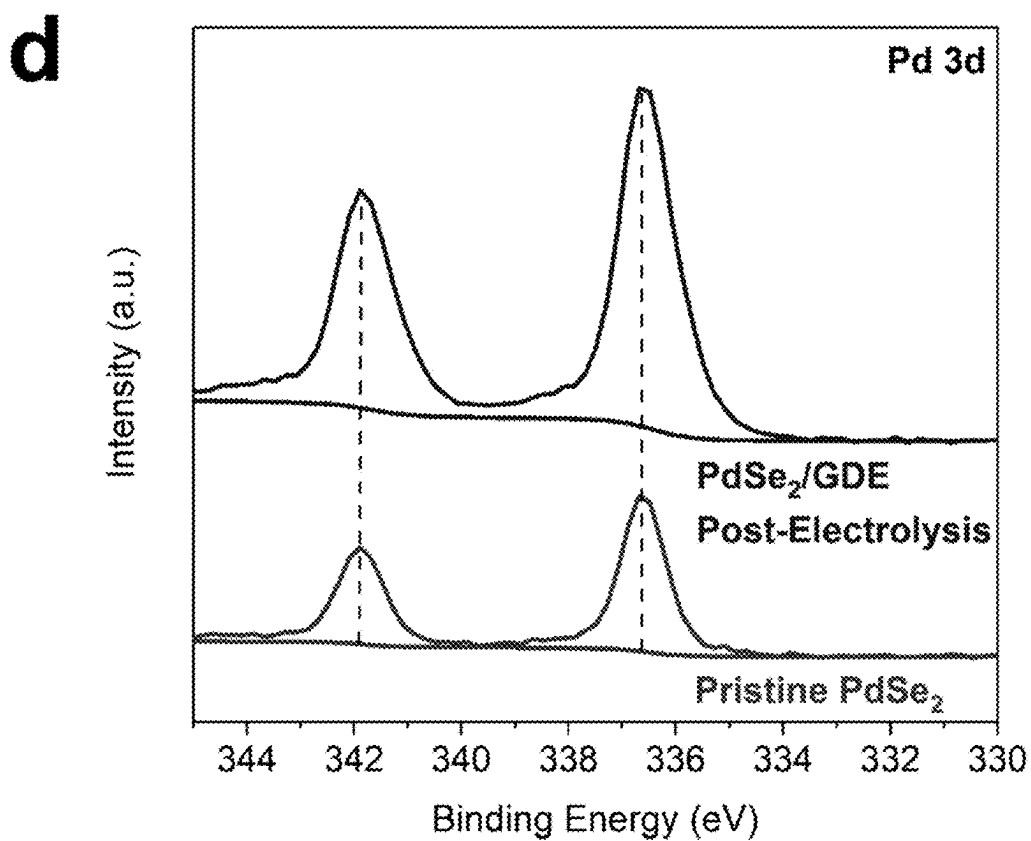
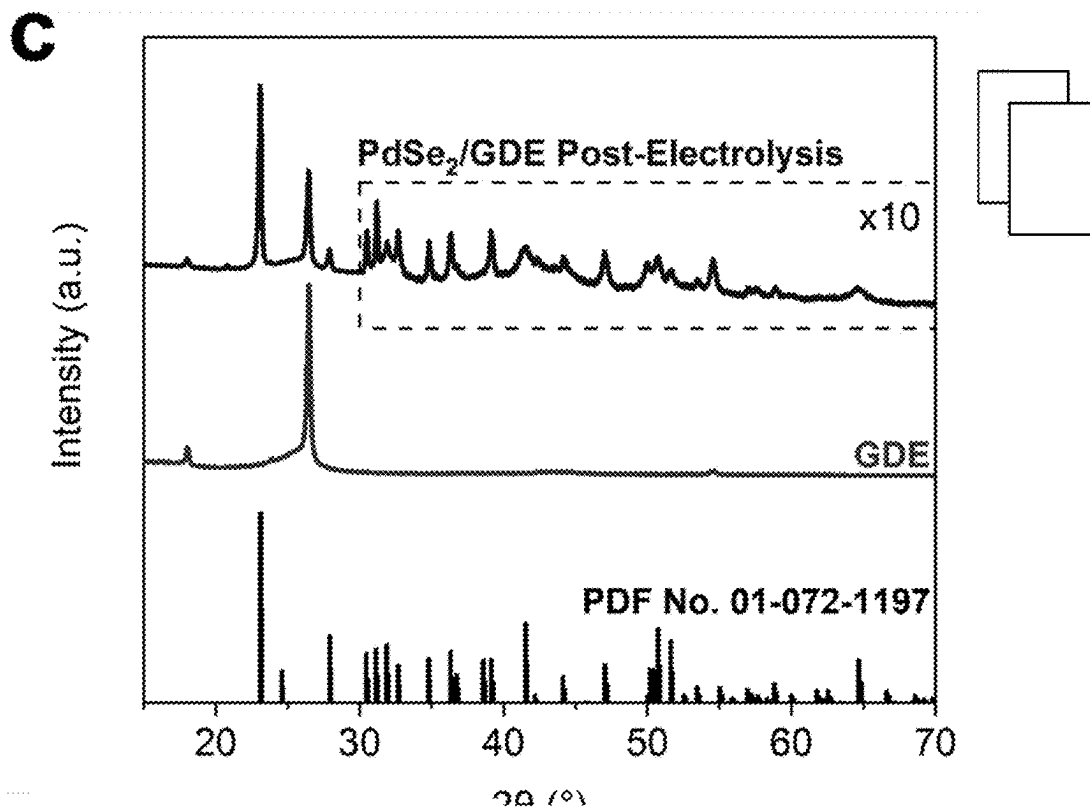


FIG. 35 Continued

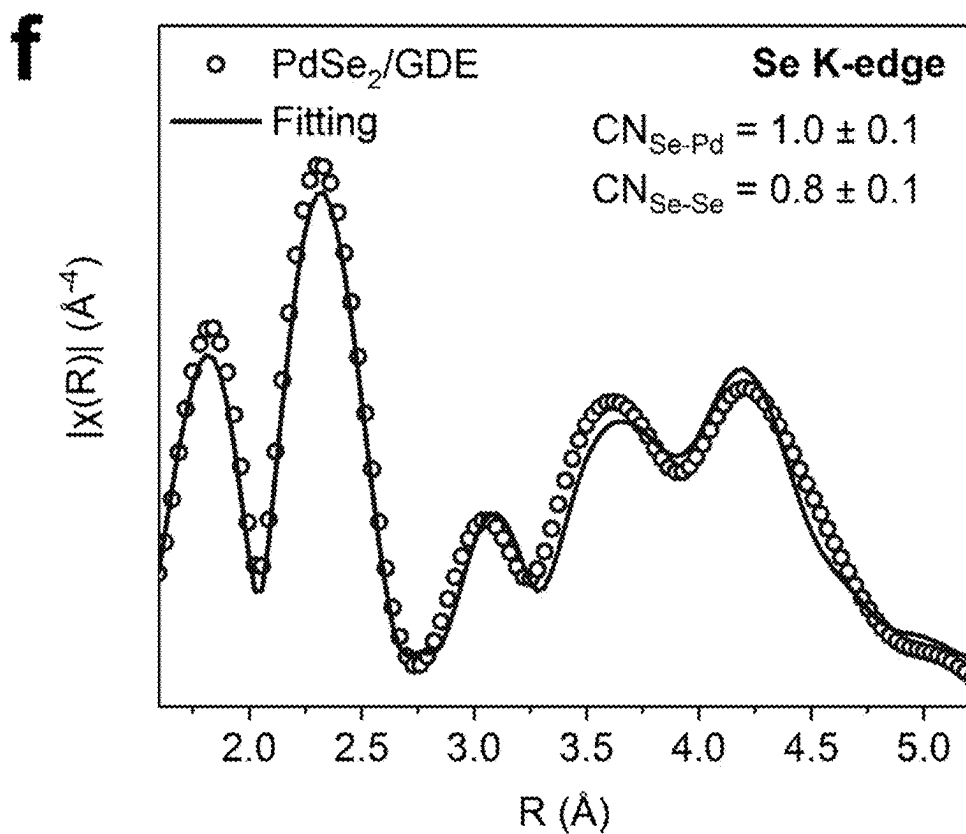
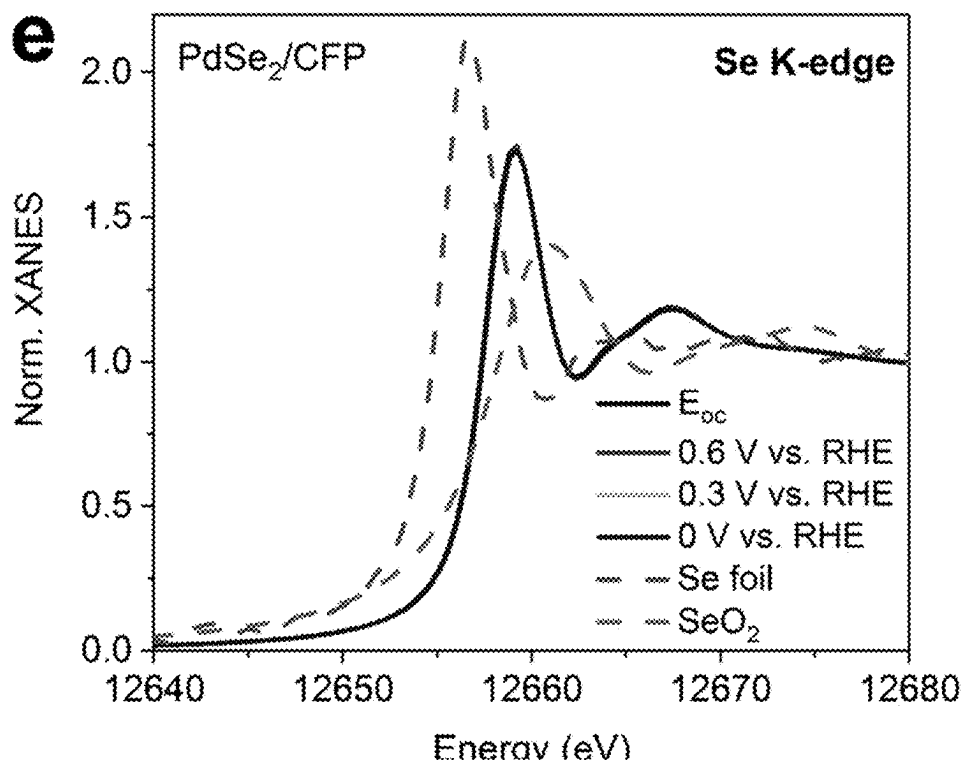
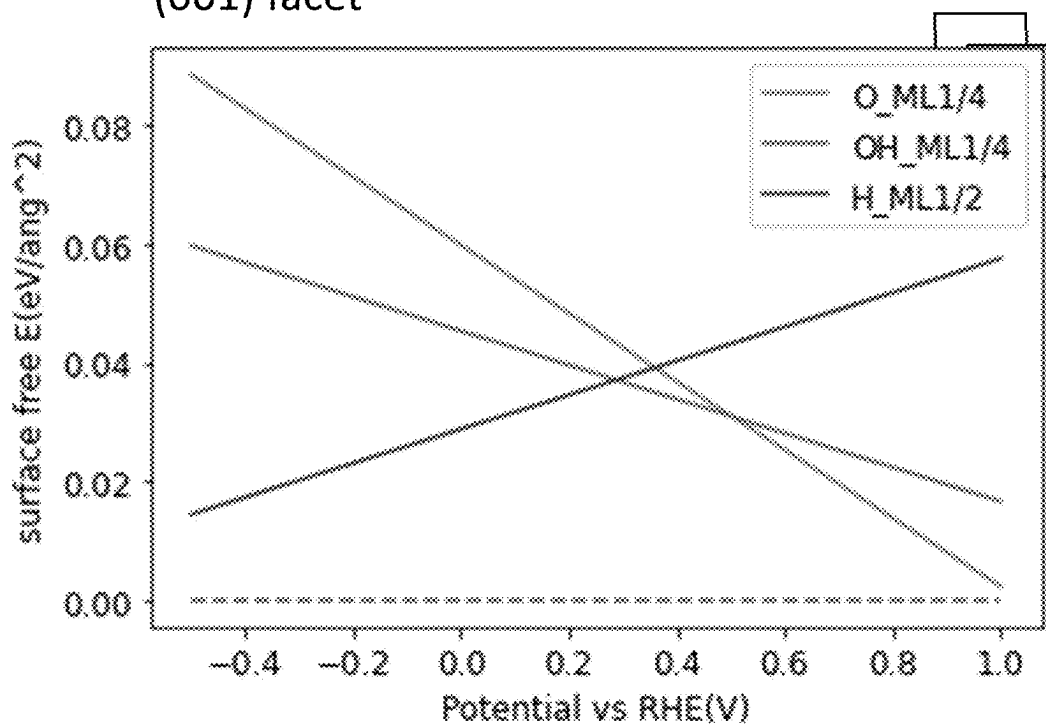


FIG. 36

(a) (001) facet



(b) (100) facet

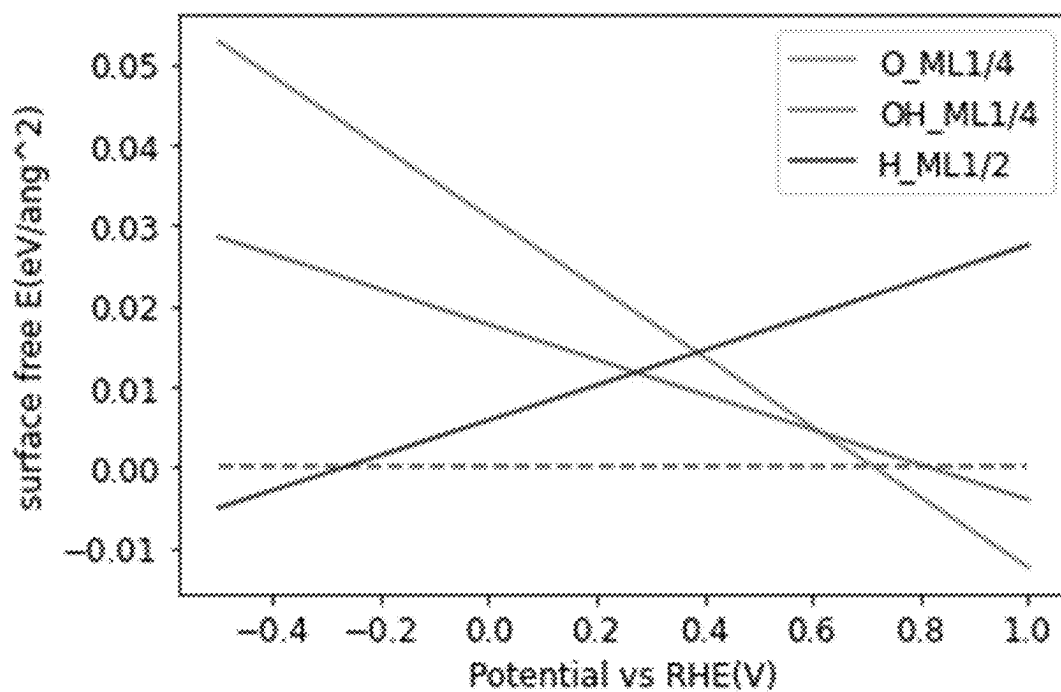
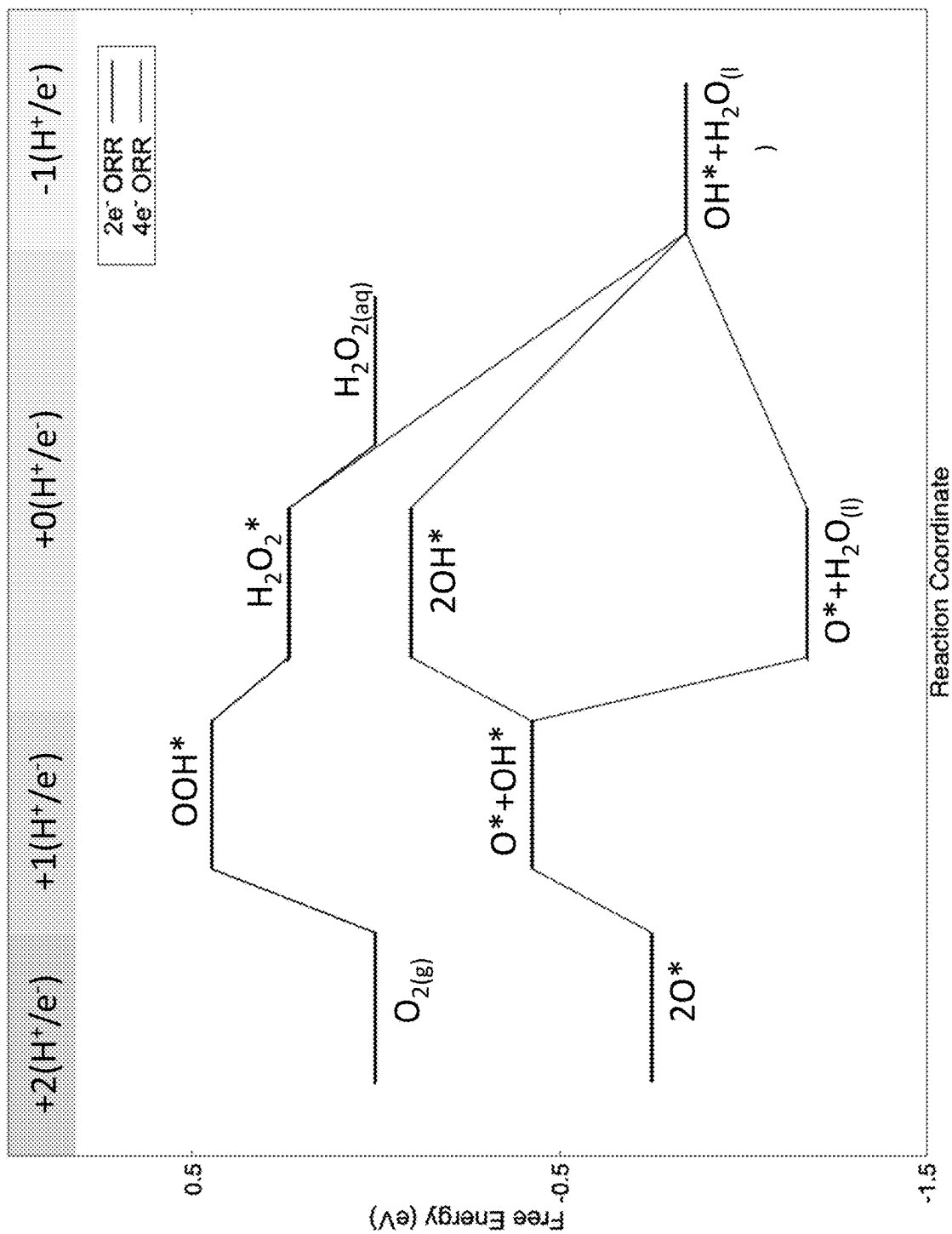


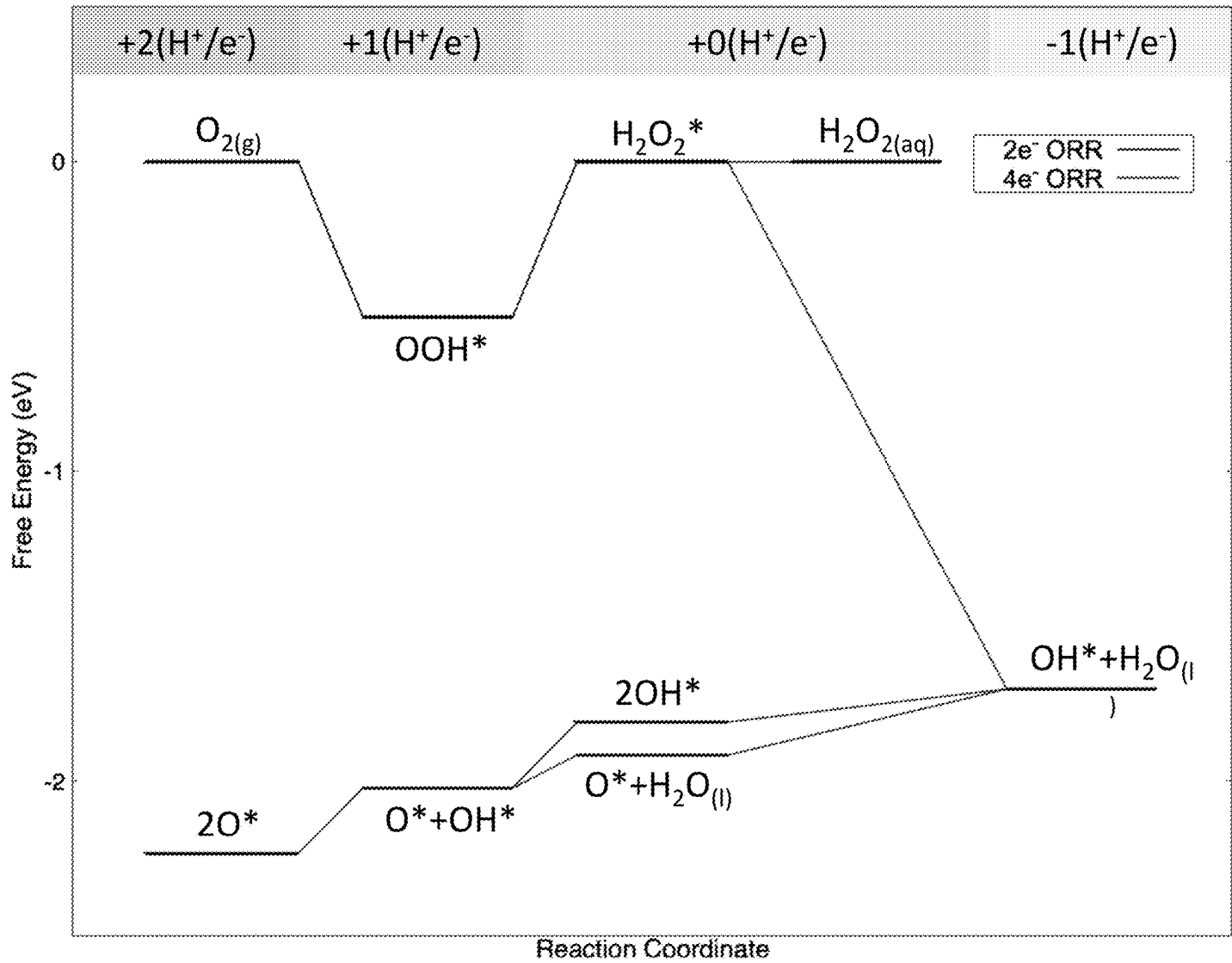
FIG. 37

(a) (001) facet



(b) (100) facet

FIG. 37 continued



]

FIG. 38

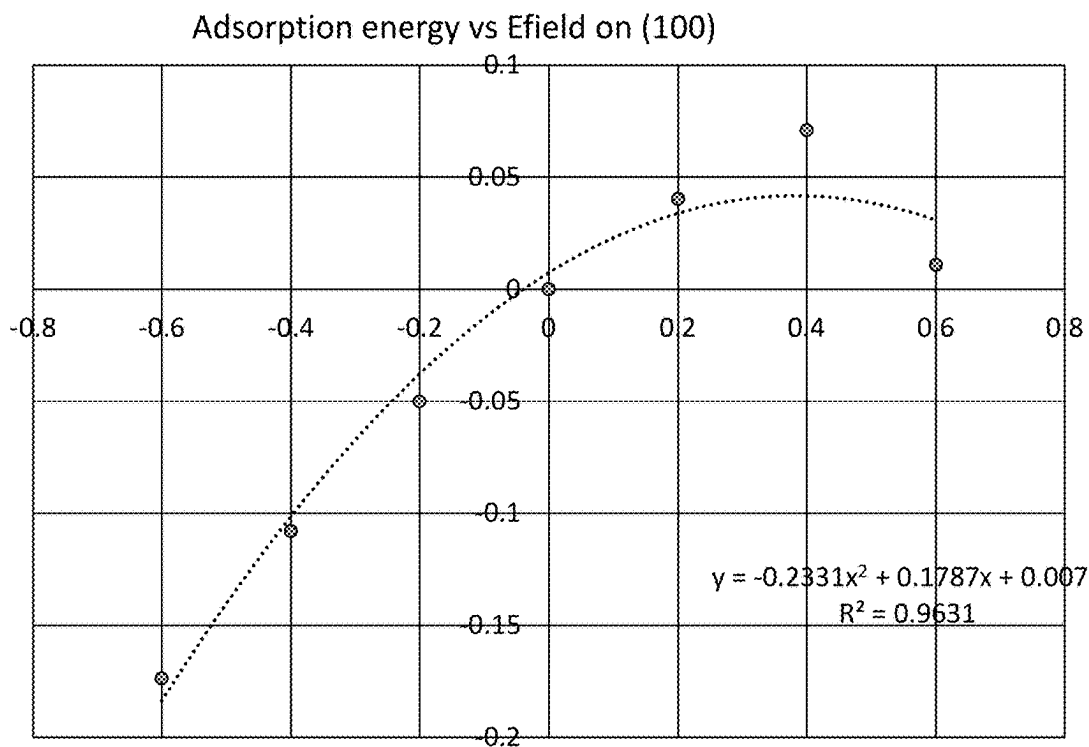
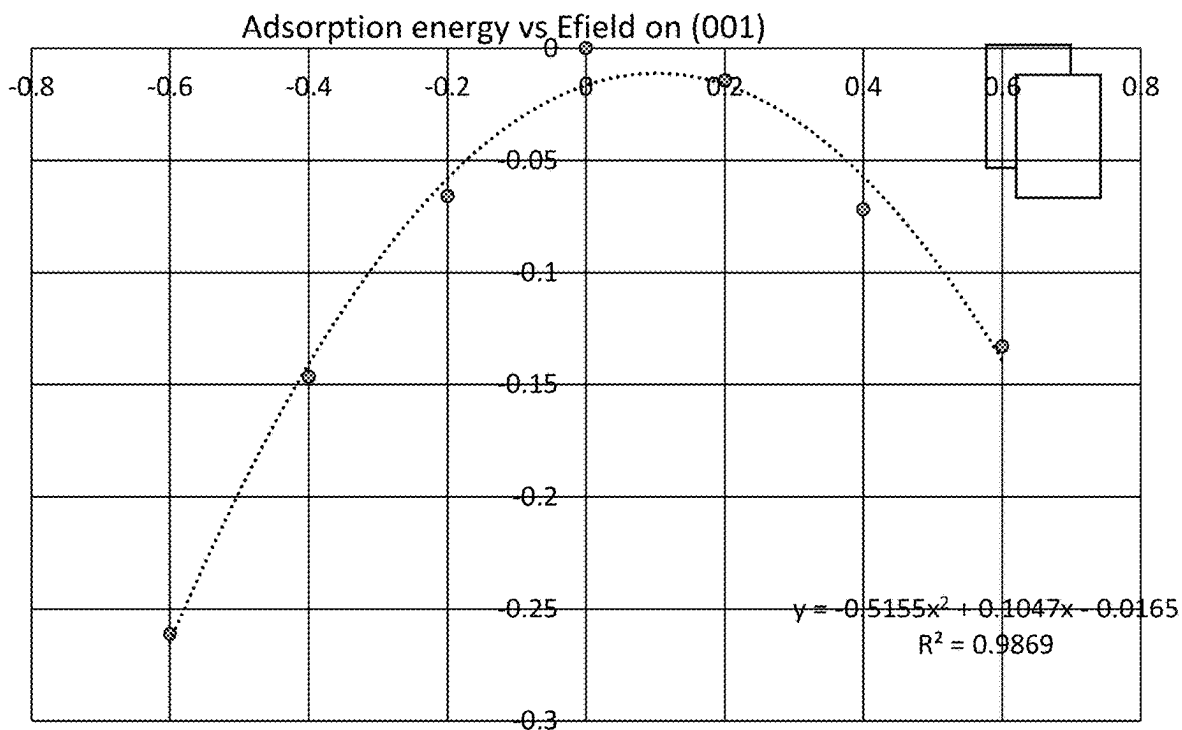


FIG. 39

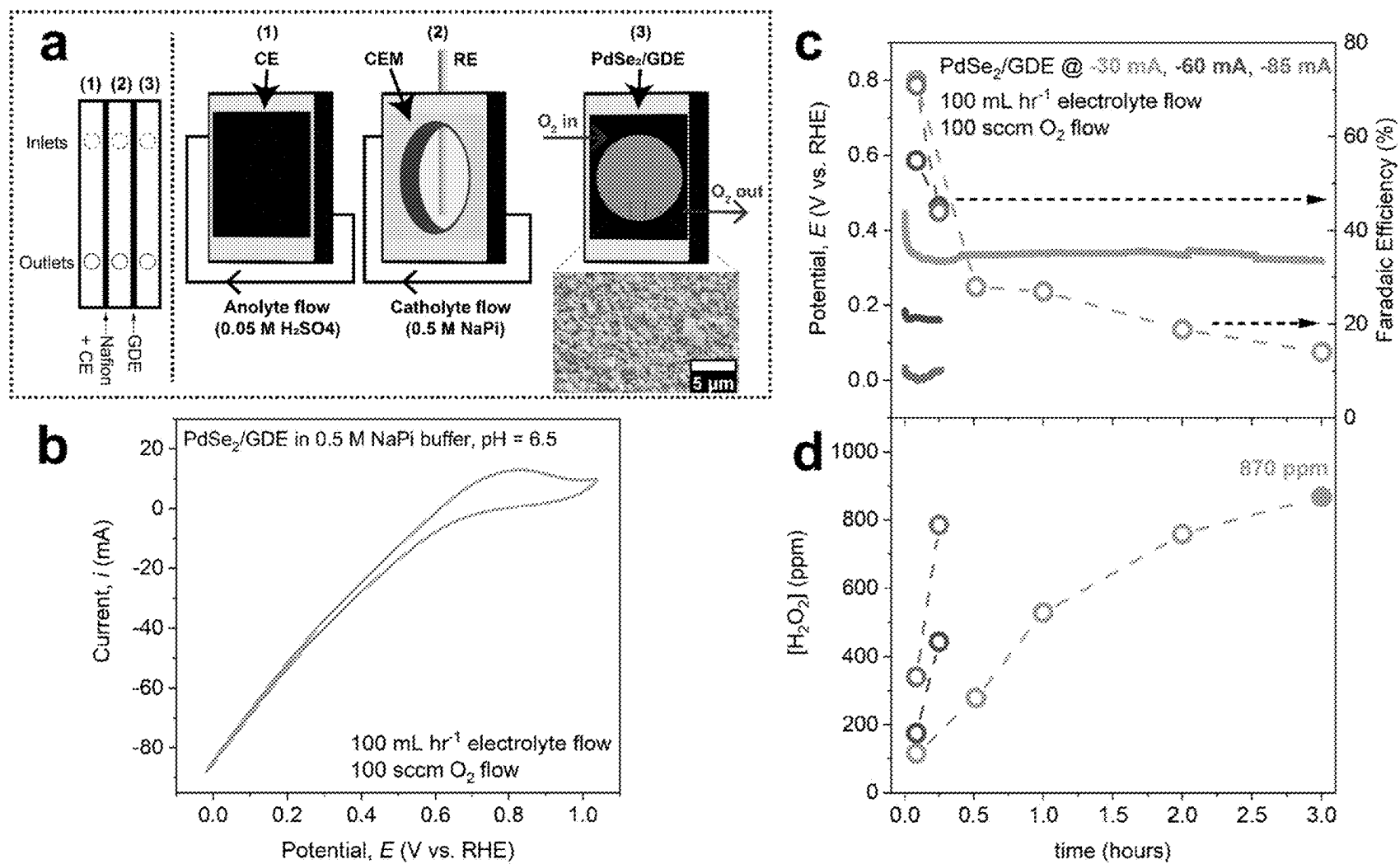
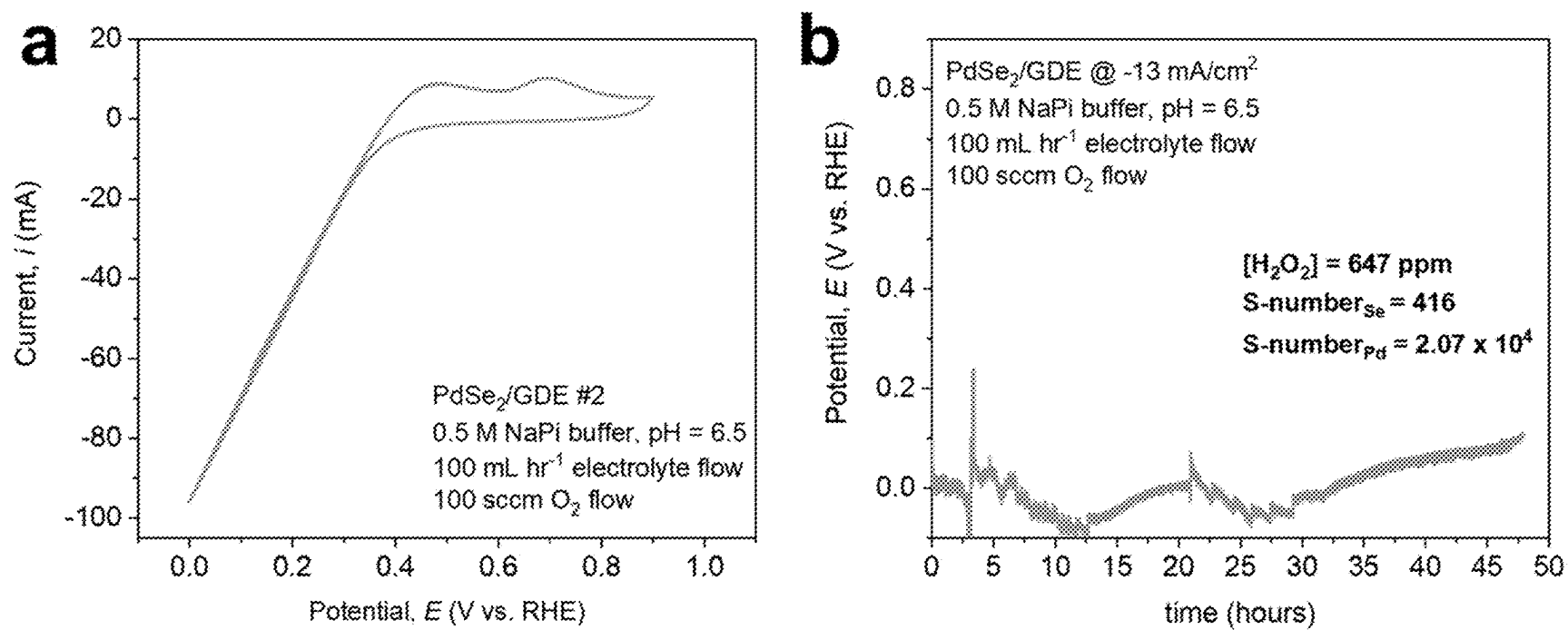


FIG. 40



**METAL COMPOUND BASED CATALYSTS
FOR ELECTROSYNTHESIS OF HYDROGEN
PEROXIDE AND LINEAR PAIRED
ELECTROCHEMICAL VALORIZATION OF
BIOMASS-DERIVED FEEDSTOCKS**

CROSS-REFERENCE TO RELATED
APPLICATIONS

[0001] This application claims priority to U.S. Provisional Application No. 63/430,933 filed on Dec. 7, 2022, the content of which is incorporated by reference in its entirety.

STATEMENT REGARDING FEDERALLY
SPONSORED RESEARCH

[0002] This invention was made with government support under 1955074 awarded by the National Science Foundation. The government has certain rights in the invention.

BACKGROUND OF THE INVENTION

[0003] Hydrogen peroxide (H_2O_2) is a powerful and green oxidant with diverse applications in chemical manufacturing, wastewater treatment, and the paper and pulp industry. The COVID-19 pandemic has also contributed to the recent growth of the global H_2O_2 market for use in disinfection. The traditional industrial production of H_2O_2 that proceeds chemically through the anthraquinone process consumes H_2 gas and is energy-intensive. It produces up to 70 wt % concentrated H_2O_2 at centralized plants and requires hazardous transportation to the point-of-use. Decentralized electrosynthesis of H_2O_2 via the two-electron oxygen reduction reaction ($2e^-$ ORR, $O_2 + 2 H^+ + 2 e^- \rightarrow H_2O_2$) offers a more sustainable route because it can be driven by increasingly affordable renewable electricity, eliminate the need for H_2 gas, and produce dilute H_2O_2 directly at the point-of-use, which is advantageous for distributed applications such as water treatment that only requires dilute (<0.1 wt %) H_2O_2 . The key challenge is to develop robust electrocatalysts with high activity, selectivity, and stability for the desired $2e^-$ reduction to H_2O_2 (vs. the competing $4e^-$ reduction to water).

[0004] Electrochemical valorization of surplus biomass-derived feedstocks, such as glycerol, into high-value chemicals offers a sustainable route for utilizing biomass resources and decarbonizing chemical manufacturing. Glycerol, for example, is typically valorized solely via anodic oxidation, with lower-value products such as hydrogen gas or water generated at cathode. However, there is a need to improve biomass utilization by valorizing biomass resources at both the anode and cathode.

BRIEF SUMMARY OF THE INVENTION

[0005] Disclosed herein are electrochemical cells and methods for using the same. One aspect of the invention provides for an electrochemical cell comprising an acidic or neutral electrolyte and a cathode immersed in the electrolyte, wherein the cathode comprises a two-electron oxygen reduction reaction ($2e^-$ ORR) electrocatalyst composed of a metal chalcogenide, wherein the metal is Ni or Pd. Another aspect of the technology provides for production of hydrogen peroxide or preparing an oxidation product of a biomass-derived feedstock with the electrochemical cell.

[0006] Another aspect of the technology provides for an electrochemical cell comprising an acidic catholyte, a cath-

ode immersed in the catholyte, an acidic anolyte, and an anode immersed in the anolyte, wherein the cathode comprises a two-electron oxygen reduction reaction ($2e^-$ ORR) electrocatalyst composed of a metal chalcogenide and the catholyte comprises oxygen (O_2), hydrogen peroxide (H_2O_2), hydroxyl radical ($\cdot OH$), a regenerable metal ion, and a biomass-derived feedstock, and wherein the anolyte comprises the biomass-derived feedstock. Another aspect of the technology provides for production of hydrogen peroxide or preparing an oxidation product of a biomass-derived feedstock with the electrochemical cell.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Non-limiting embodiments of the present invention will be described by way of example with reference to the accompanying figures, which are schematic and are not intended to be drawn to scale. In the figures, each identical or nearly identical component illustrated is typically represented by a single numeral. For purposes of clarity, not every component is labeled in every figure, nor is every component of each embodiment of the invention shown where illustration is not necessary to allow those of ordinary skill in the art to understand the invention.

[0008] FIG. 1: Linear pairing strategy for electrochemical valorization of glycerol. The schematic shows cathodic valorization of glycerol enabled by the electro-Fenton process at a stable cathode is further paired with anodic oxidation and integrated into a linear paired electrochemical process to concurrently produce the same glycerol-derived oxidation products at both cathode and anode.

[0009] FIG. 2: Computational assessments of the ORR energetics and the surface stability of c-NiSe₂ (in comparison with c-CoSe₂). Panel (a) shows crystal structures of c-NiSe₂ and c-CoSe₂. Panel (b) shows calculated free energy diagrams of the $2e^-$ vs. $4e^-$ ORR pathway on the c-NiSe₂ vs. c-CoSe₂ (100) surface at U_{RHE}° . Panel (c) shows different coverages of O* and/or OH* (top) and comparisons of their free energies (bottom) on the c-NiSe₂ vs. c-CoSe₂ (100) surface in equilibrium with water. The binding energies of O* and OH* on their preferential binding sites at U_{RHE}° are shown as the bottom insets in panel c. The yellow shaded regions indicate the potential range where the adsorbate-free clean surface is lower in free energy compared to the O*-and/or OH*-adsorbed surfaces. The inset images show the co-adsorption of one O* and one OH* to their preferential binding sites on the surface unit cell including two metal sites and four Se sites. The Ni, Co, Se, O, and H atoms are displayed in green, magenta, orange, red, and white, respectively.

[0010] FIG. 3: The electrocatalytic properties and stability of c-NiSe₂ (in comparison with c-CoSe₂) for acidic $2e^-$ ORR and bulk electrosynthesis of H_2O_2 . Panel (a) shows RRDE voltammograms recorded at 1600 rpm and panel (b) shows the H_2O_2 selectivity profiles of drop-casted c-NiSe₂ (left) and c-CoSe₂ (right) catalysts with various catalyst loadings in O_2 -saturated 0.05 M H_2SO_4 (pH~1.2). Panel (c) shows normalized metal and selenium leaching rates of drop-casted c-NiSe₂ and c-CoSe₂ catalysts during RRDE stability tests in O_2 -saturated 0.05 M H_2SO_4 (pH~1.2, left) and 0.1 M $NaHSO_4/Na_2SO_4$ buffer (pH~2.8, right). For each catalyst, the error bars result from four RRDE stability tests at different catalyst loadings (Table 2). Panel (d) shows the cumulative H_2O_2 yield (left) and H_2O_2 selectivity (right) after 6 hours for four trials of H_2O_2 bulk electrosynthesis in

O₂-saturated 0.05 M H₂SO₄ (4 mL, stirred at 1200 rpm) using four NiSe₂/CFP electrodes ($\sim 1.06 \text{ mg}_{\text{Ni}} \text{ cm}^{-2}_{\text{geo}}$, $\sim 1 \text{ cm}^{-2}_{\text{geo}}$) operated at different fixed applied potentials (0.50, 0.55, 0.60, 0.65 V vs. RHE) (see details in FIG. 18). Panel (e) show long-term (37 h) sustained bulk electrosynthesis of H₂O₂ in O₂-saturated 0.05 M H₂SO₄ at the optimum potential of 0.60 V vs. RHE using one NiSe₂/CFP electrode repeatedly for five consecutive runs (see details in FIG. 21).

[0011] FIG. 4: Glycerol valorization enabled by the electro-Fenton process on NiSe₂/CFP in the cathodic half-cell. Panel (a) shows balanced equation of cathodic glycerol valorization, which suggests proton consumption. Panel (b) shows possible reaction pathways of glycerol oxidation into various C₃, C₂, and C₁ products by the electro-Fenton process at NiSe₂/CFP cathode. The detected (or anticipated) and undetected products are labeled based on NMR analyses. Panel (c) shows glycerol conversion (left) and the selectivity toward all detected C₃ products (right) as a function of [Fe²⁺] (0.1, 0.5, 1.0, or 2.5 mM) after passing a controlled amount of charge through NiSe₂/CFP cathode in O₂-saturated 0.1 M NaHSO₄/Na₂SO₄ buffer (pH \sim 2.8) starting with \sim 50 mM glycerol under vigorous stirring. Panel (c) shows aqueous phase organic (C₃, C₂, and C₁) product selectivity, glycerol conversion percentage, and carbon balance of all detected aqueous phase organic products for cathodic valorization of glycerol (\sim 50 mM) under the optimum [Fe²⁺] of 0.5 mM.

[0012] FIG. 5: Linear paired electrochemical valorization of glycerol via the electro-Fenton process at NiSe₂/CFP cathode and oxidation at Pt/C anode. Panel (a) shows the cathode current and external bias over time, which shows the steady operation of the linear paired system including a NiSe₂/CFP cathode ($\sim 1.24 \text{ mg}_{\text{Ni}} \text{ cm}^{-2}_{\text{geo}}$, $\sim 1 \text{ cm}^{-2}_{\text{geo}}$) operated at 0.60 V vs. RHE in O₂-saturated NaHSO₄/Na₂SO₄ buffer (pH \sim 2.8, containing \sim 50 mM glycerol and 0.5 mM Fe²⁺) and a Pt/C anode ($\sim 2 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}_{\text{geo}}$, $\sim 1 \text{ cm}^{-2}_{\text{geo}}$) operated in Ar-saturated H₂SO₄ solution (containing \sim 50 mM glycerol). The current and bias are influenced by different supporting electrolyte concentrations (Condition I: 0.1 M NaHSO₄/Na₂SO₄ for catholyte, and 0.05 M H₂SO₄ for anolyte; Condition II: 0.5 M NaHSO₄/Na₂SO₄ for catholyte, and 0.5 M H₂SO₄ for anolyte). Panel (b) shows product selectivity, glycerol conversion percentage, and carbon balance of all detected aqueous phase organic (C₃, C₂, and C₁) products for linear paired electrochemical valorization of glycerol under different supporting electrolyte conditions (I and II, as described in panel a).

[0013] FIG. 6: Calculated bulk Pourbaix diagrams. Panel (a) shows c-NiSe₂ and panel (b) shows c-CoSe₂ assuming an ionic concentration of 10⁻⁶ mol/kg for each element of interest (59 ppb Ni, 59 ppb Co, and 79 ppb Se, which are reasonably low concentrations that can fairly reflect the acidic electrolyte solutions used in our experiments). These diagrams are adapted from the Materials Project^{S1}. The multicolor gradient indicates the Gibbs free energy of the compound at a given set of potential and pH conditions with respect to its Pourbaix stable phase (ΔG_{pbx}), reflecting the electrochemical stability window of the compound. It was surmised in a previous report^{S2} that materials with ΔG_{pbx} up to high values as much as 0.5 eV/atom can persist in electrochemical environments because of the energy barriers for the dissociation reactions. The solid white frame defines the thermodynamic equilibrium stability window of the compound without considering the kinetics of the dissocia-

tion reactions. The yellow and orange color vertical bars indicate the potential and pH ranges of interest for the acidic 2e⁻ ORR (in 0.05 M H₂SO₄) and for the Fe²⁺-mediated electro-Fenton process (at the optimum pH of 2.8 to 3.0), respectively.

[0014] FIG. 7: Panel (a) shows SEM image of Ni(OH)₂ precursor. Panel (b) shows SEM image, panel (c) shows PXRD pattern, panel (d) shows Raman spectrum, panel (e) shows Ni 2p and panel (f) shows Se 3d XPS spectra of as-synthesized c-NiSe₂ sample. The standard PXRD pattern of c-NiSe₂ (PDF #88-1711) is adapted from the International Centre for Diffraction Data (ICDD) database. From the structural characterization results, the as-synthesized c-NiSe₂ sample is phase-pure and exhibits unoxidized surface.

[0015] FIG. 8: Panel (a) shows SEM image of CHCH precursor. Panel (b) shows SEM image, Panel (c) shows PXRD pattern, panel (d) shows Raman spectrum, panel (e) shows Co 2p and panel (f) shows Se 3d XPS spectra of as-synthesized c-CoSe₂ sample. The standard PXRD pattern of c-CoSe₂ (PDF #88-1712) is adapted from the International Centre for Diffraction Data (ICDD) database. From the structural characterization results, the as-synthesized c-CoSe₂ sample is phase-pure and exhibits unoxidized surface.

[0016] FIG. 9: Cyclic voltammograms of c-NiSe₂ in panels (a-d) and c-CoSe₂ in panels (e-h) catalysts with various catalyst loadings recorded in Ar-saturated 0.05 M H₂SO₄ solution (pH \sim 1.2) at various scan rates. The corresponding C_{dl} values of (i) c-NiSe₂ and (j) c-CoSe₂ catalysts with various catalyst loadings at 0.35 V vs. RHE in Ar-saturated 0.05 M H₂SO₄ solution (pH \sim 1.2). (k) Various catalyst loadings of c-NiSe₂ and c-CoSe₂ catalysts result in similar ranges of C_{dl} values between these two catalysts at 0.35 V vs. RHE in Ar-saturated 0.05 M H₂SO₄ solution.

[0017] FIG. 10: Panel (a) shows RRDE voltammograms recorded at 1600 rpm and panel (b) shows the H₂O₂ selectivity profiles of drop-casted c-NiSe₂ (left) and c-CoSe₂ (right) catalyst with various catalyst loadings in O₂-saturated 0.1 M NaHSO₄/Na₂SO₄ buffer solution (pH \sim 2.8, the optimal pH for the electro-Fenton process).

[0018] FIG. 11: Cyclic voltammograms of c-NiSe₂ in panels (a-d) and c-CoSe₂ in panels (e-h) catalysts with various catalyst loadings recorded in Ar-saturated 0.1 M NaHSO₄/Na₂SO₄ buffer solution (pH \sim 2.8) at various scan rates. The corresponding C_{dl} values of c-NiSe₂ in panel (i) and c-CoSe₂ in panel (j) catalysts with various catalyst loadings at 0.35 V vs. RHE in Ar-saturated 0.1 M NaHSO₄/Na₂SO₄ buffer solution (pH \sim 2.8). Panel (k) shows various catalyst loadings of c-NiSe₂ and c-CoSe₂ catalysts result in similar ranges of C_{dl} values between these two catalysts at 0.35 V vs. RHE in Ar-saturated 0.1 M NaHSO₄/Na₂SO₄ buffer solution.

[0019] FIG. 12: Protocols for the RRDE stability tests of c-NiSe₂ and c-CoSe₂ catalysts. Step 1 (red shaded region): In O₂-saturated electrolyte solution, the Pt ring electrode was electrochemically cleaned by running cyclic voltammetry between 0.05 V and 1.2 V vs. RHE (without iR-correction) at the scan rate of 100 mV s⁻¹ and the rotation rate of 1600 rpm for 10 cycles, meanwhile holding the catalyst-coated disk electrode at 0.75 V vs. RHE. The purpose of this step is to remove PtO_x from the Pt ring electrode surface^{S3, S4}.

[0020] Step 2 (blue shaded region): In O₂-saturated electrolyte solution, the catalyst-coated disk electrode was linearly swept from 0.75 V to -0.025 vs. RHE (without iR-correction) at the scan rate of 50 mV s⁻¹ and a constant rotation rate (400, 625, 900, 1225, 1600, or 2025 rpm) to drive the acidic 2e⁻ ORR, meanwhile holding the Pt ring electrode at 1.3 V vs. RHE to detect the H₂O₂ production. The rotation rate was sequentially changed between scans.

[0021] Overall procedure: Since holding the Pt ring electrode at 1.3 V vs. RHE for an extended period of time in Step 2 would result in the formation of the surface PtO_x^{S3, S4}, the Pt ring electrode was periodically cleaned during the RRDE stability tests using the protocol described in Step 1. Thus, the RRDE stability tests were performed by alternating between Step 1 and Step 2, leading to a total of 255 linear sweep voltammetry scans on the disk electrode over the entire course of ~4.0 h. The catalyst stability was monitored by tracking the disk potential required at a certain disk current density (j_{disk}) or peroxide current density ($j_{peroxide}$) of 0.5 mA cm⁻²_{disk} at 2025 rpm (FIGS. 13 and 14).

[0022] FIG. 13: The stability of c-NiSe₂ shown in panel (a) and c-CoSe₂ shown in panel (b) catalysts with various catalyst loadings monitored by tracking the disk potential at a certain disk current density (j_{disk} , top) or peroxide current density ($j_{peroxide}$, bottom) of 0.5 mA cm⁻²_{disk} at 2025 rpm during the RRDE stability tests in O₂-saturated 0.05 M H₂SO₄ solution (pH~1.2). The red shaded regions refer to the electrochemical cleaning of the Pt ring electrode, and the blue shaded regions refer to the linear sweep voltammetry of the catalyst-coated disk electrode (see details in FIG. 12). The disk potential of c-NiSe₂ remained stable to reach the same magnitude of j_{disk} or $j_{peroxide}$ throughout the tests (panel a), whereas that of c-CoSe₂ cathodically shifted over the scans (panel b).

[0023] FIG. 14: The stability of c-NiSe₂ shown in panel (a) and c-CoSe₂ shown in panel (b) catalysts with various catalyst loadings monitored by tracking the disk potential at a certain disk current density (j_{disk} , top) or peroxide current density ($j_{peroxide}$, bottom) of 0.5 mA cm⁻²_{disk} at 2025 rpm during the RRDE stability tests in O₂-saturated 0.1 M NaHSO₄/Na₂SO₄ buffer solution (pH~2.8, optimal for the electro-Fenton process). The red shaded regions refer to the electrochemical cleaning of the Pt ring electrode, and the blue shaded regions refer to the linear sweep voltammetry of the catalyst-coated disk electrode (see details in FIG. 12). The disk potential of c-NiSe₂ remained stable to reach the same magnitude of j_{disk} or $j_{peroxide}$ throughout the tests (panel a), whereas that of c-CoSe₂ cathodically shifted over the scans (panel b).

[0024] FIG. 15: Panels (a,b) show Raman spectra of (a) c-NiSe₂ and (b) c-CoSe₂ catalysts before and after RRDE stability tests in O₂-saturated 0.05 M H₂SO₄ (pH~1.2) or 0.1 M NaHSO₄/Na₂SO₄ (pH~2.8), showing no change after electrochemical testing. (c,d) X-ray photoelectron spectra of (c) c-NiSe₂ and (d) c-CoSe₂ catalysts before and after RRDE stability tests in O₂-saturated 0.05 M H₂SO₄ (pH~1.2) or 0.1 M NaHSO₄/Na₂SO₄ (pH~2.8). The Ni 2p spectra of the spent c-NiSe₂ catalyst were interfered by the F KL2 Auger signal because of the presence of Nafion in the recovered catalyst (panel c, left). Since the Se 3d spectra of the spent c-NiSe₂ catalyst (panel c, right) and the Co 2p and Se 3d spectra of the spent c-CoSe₂ catalyst (panel d) showed no change after electrochemical testing, it can be concluded that

the surface chemical states of the spent c-NiSe₂ and c-CoSe₂ catalysts remained the same as those of the pristine samples.

[0025] FIG. 16: Panel (a) shows SEM image of Ni(OH)₂/CFP precursor. Panel (b) shows SEM image, panel (c) shows PXRD pattern, panel (d) shows Raman spectrum, panel (e) shows Ni 2p and panel (f) shows Se 3d XPS spectra of as-synthesized c-NiSe₂/CFP sample. The asterisks in (c) indicate the PXRD peaks of the CFP substrate. The standard PXRD pattern of c-NiSe₂ (PDF #88-1711) is adapted from the International Centre for Diffraction Data (ICDD) database. From the structural characterization results, the as-synthesized c-NiSe₂/CFP sample is phase-pure and exhibits unoxidized surface.

[0026] FIG. 17: Shows a schematic of the two-compartment three-electrode setup for bulk electroynthesis of H₂O₂ in acidic solution. Nafion 117 membrane was used to separate the two compartments to avoid the oxidation of H₂O₂ product on the anode. A minimal volume (4 mL) of catholyte was used and vigorously stirred at 1200 rpm to achieve higher H₂O₂ concentrations under facilitated mass transfer of O₂ gas. A blanket of O₂ gas was maintained over the surface of O₂-saturated catholyte during H₂O₂ electroynthesis. A rubber septum punctured with a syringe needle served as the gas outlet, which was only removed when a small aliquot of catholyte was sampled for chemical detection of H₂O₂ product and was otherwise capped to minimize the evaporation of catholyte during H₂O₂ electroynthesis.

[0027] FIG. 18: Bulk electroynthesis of H₂O₂ in O₂-saturated 0.05 M H₂SO₄ solution (pH~1.2, 4 mL, stirred at 1200 rpm) using four c-NiSe₂/CFP electrodes (~1.06 mg_{Ni} cm⁻²_{geo}, ~1 cm⁻²_{geo}) operated at four different fixed applied potentials (0.65 V, 0.60 V, 0.55 V, 0.50 V vs. RHE). Panel (a) shows chronoamperometry curves, cumulative H₂O₂ concentration, cumulative H₂O₂ yield, cumulative H₂O₂ selectivity and Faradaic efficiency as a function of time. Comparisons of the cumulative H₂O₂ yield and H₂O₂ selectivity at the 6 h mark of each trial are shown in FIG. 3d. Panel (b) shows cyclic voltammograms of the c-NiSe₂/CFP electrodes recorded before and after each trial of the H₂O₂ electroynthesis in O₂-saturated 0.05 M H₂SO₄ solution (stirred at 1200 rpm).

[0028] FIG. 19: Panel (a) shows RRDE voltammograms of c-NiSe₂ (left, 458 μg_{Ni} cm⁻²_{disk}) and c-CoSe₂ (right, 229 μg_{Co} cm⁻²_{disk}) catalysts recorded at 1600 rpm in O₂-saturated 0.05 M H₂SO₄ solution (pH~1.2) were performed to study the 2e⁻ ORR (j_{disk} : disk current density; j_{ring} : ring current density; $j_{peroxide}$: peroxide current density). C_{dl} values of c-NiSe₂ (304 μF cm⁻²_{disk}) and c-CoSe₂ (365 μF cm⁻²_{disk}) was evaluated at 0.35 V vs. RHE in the same solution under Ar saturation. Linear sweep voltammograms of the catalyst-coated disk electrode recorded at 1600 rpm in Ar-saturated 0.05 M H₂SO₄ solution (pH~1.2) containing 1 mM, 5 mM, 10 mM, or 20 mM H₂O₂ were performed to study the electroreduction of H₂O₂ (j_{PRR} : current density of the hydrogen peroxide reduction reaction). The shaded regions (green: c-NiSe₂; magenta: c-CoSe₂) define the potential range where the magnitude of $j_{peroxide}$ under O₂ saturation (~1 mM O₂) was greater than that of j_{PRR} under 20 mM H₂O₂. Panel (b) shows $j_{peroxide} - j_{PRR}$ plotted against potential under 0 mM H₂O₂ (dashed lines, where $j_{PRR}=0$) or 20 mM H₂O₂ (solid lines). The shaded regions in (b) have the same physical meanings as those in (a). Compared to c-CoSe₂, the H₂O₂ production on c-NiSe₂ was more affected by the H₂O₂ electroreduction, as reflected by the greater

decrease in the peak value of $j_{peroxide} - j_{PRR}$ when the H_2O_2 concentration increased from 0 mM to 20 mM.

[0029] FIG. 20: Panel (a) shows RRDE voltammograms of c-NiSe₂ (left, 381 $\mu g_{Ni} cm^{-2}_{disk}$) and c-CoSe₂ (right, 229 $\mu g_{Co} cm^{-2}_{disk}$) catalysts recorded at 1600 rpm in O₂-saturated 0.1 M NaHSO₄/Na₂SO₄ solution (pH~2.8) were performed to study the 2e⁻ ORR (j_{disk} : disk current density; j_{ring} : ring current density; $j_{peroxide}$: peroxide current density). C_{dl} values of c-NiSe₂ (328 $\mu F cm^{-2}_{disk}$) and c-CoSe₂ (337 $\mu F cm^{-2}_{disk}$) was evaluated at 0.35 V vs. RHE in the same solution under Ar saturation. Linear sweep voltammograms of the catalyst-coated disk electrode recorded at 1600 rpm in Ar-saturated 0.1 M NaHSO₄/Na₂SO₄ solution (pH~2.8) containing 1 mM, 5 mM, 10 mM, or 20 mM H₂O₂ were performed to study the electroreduction of H₂O₂ (j_{PRR} : current density of the hydrogen peroxide reduction reaction). The shaded regions (green: c-NiSe₂; magenta: c-CoSe₂) define the potential range where the magnitude of $j_{peroxide}$ under O₂ saturation (~1 mM O₂) was greater than that of j_{PRR} under 20 mM H₂O₂. Panel (b) shows $j_{peroxide} - j_{PRR}$ plotted against potential under 0 mM H₂O₂ (where $j_{PRR} = 0$, dashed lines) or 20 mM H₂O₂ (solid lines). The shaded regions in (b) have the same physical meanings as those in (a). Compared to c-CoSe₂, the H₂O₂ production on c-NiSe₂ was more affected by the H₂O₂ electroreduction, as reflected by the greater decrease in the peak value of $j_{peroxide} - j_{PRR}$ when the H₂O₂ concentration increased from 0 mM to 20 mM.

[0030] FIG. 21: Bulk electrosynthesis of H₂O₂ in O₂-saturated 0.05 M H₂SO₄ solution (pH~1.2, 4 mL, stirred at 1200 rpm) at the optimum potential of 0.60 V vs. RHE using one c-NiSe₂/CFP electrode (~1.06 $mg_{Ni} cm^{-2}_{geo}$, ~1 cm^{-2}_{geo}) repeatedly for five consecutive runs and a total of 37 hours. Panel (a) shows chronoamperometry curve. Panel (b) shows cumulative H₂O₂ concentration, panel (c) shows cumulative H₂O₂ yield, panel (d) shows cumulative H₂O₂ selectivity and Faradaic efficiency as a function of time. Fresh H₂O₂-free electrolyte solution was replaced into the cathode compartment between runs. Comparisons of the cumulative H₂O₂ yield and H₂O₂ selectivity at the 2 h mark and the end of each run are shown in FIG. 3e.

[0031] FIG. 22: Bulk electrosynthesis of H₂O₂ in O₂-saturated 0.1 M NaHSO₄/Na₂SO₄ solution (pH~2.8, 4 mL, stirred at 1200 rpm) using c-NiSe₂/CFP electrode (~1.06 $mg_{Ni} cm^{-2}_{geo}$, ~1 cm^{-2}_{geo}) operated at 0.60 vs. RHE. Shows chronoamperometry curve, cumulative H₂O₂ concentration, cumulative H₂O₂ yield, and cumulative H₂O₂ selectivity and Faradaic efficiency as a function of time.

[0032] FIG. 23: Panel (a) shows Raman spectra and panel (b) shows X-ray photoelectron spectra of c-NiSe₂/CFP before and after H₂O₂ bulk electrosynthesis at 0.60 V vs. RHE in O₂-saturated 0.05 M H₂SO₄ or 0.1 M NaHSO₄/Na₂SO₄. Panel (c) shows Ni K-edge and Se K-edge X-ray absorption near edge structure (XANES, left) and extended X-ray absorption fine structure (EXAFS, right) spectra of c-NiSe₂/CFP before and after H₂O₂ bulk electrosynthesis at 0.60 V vs. RHE in O₂-saturated 0.05 M H₂SO₄, which are nearly identical. Panel (d) shows normalized nickel and selenium leaching rates of c-NiSe₂/CFP (~1.06 $\mu g_{Ni} cm^{-2}_{geo}$, ~1 cm^{-2}_{geo}) during H₂O₂ bulk electrosynthesis at 0.60 V vs. RHE in O₂-saturated 0.05 M H₂SO₄ or 0.1 M NaHSO₄/Na₂SO₄.

[0033] FIG. 24: Shows schematic of the two-compartment three-electrode setup for half-cell studies of the electro-Fenton process for glycerol valorization at c-NiSe₂ cathode.

[0034] FIG. 25: Panel (a) shows chronoamperometry curves when passing a controlled amount of charge (14.6 C, 29.2 C, or 43.9 C) through the c-NiSe₂ cathode (~1.06 $mg_{Ni} cm^{-2}_{geo}$, ~1 cm^{-2}_{geo}) at 0.60 V vs. RHE in 4 mL of O₂-saturated 0.1 M NaHSO₄/Na₂SO₄ solution (pH~2.8, stirred at 1200 rpm) containing ~50 mM glycerol and 0.5 mM Fe²⁺. Panel (b) shows ¹H NMR spectra before and after passing a controlled amount of charge through the c-NiSe₂ cathode. Each NMR sample in (b) was made by mixing 25 μL of D₂O (containing the maleic acid internal standard) with 475 μL of aqueous catholyte, and the final concentration of the maleic acid internal standard after mixing is ~5 mM. As the amount of passed charge increased, the solution volume in the cathode compartment decreased due to evaporation under the O₂ gas flow, the solution pH in the cathode compartment decreased due to proton permeation from the more acidic 0.05 M H₂SO₄ solution in the anode compartment (see FIG. 24). Panel (c) shows aqueous phase organic (C₃, C₂, and C₁) product selectivity, glycerol conversion percentage, and carbon balance of all detected aqueous phase organic products determined by ¹H NMR results after passing a controlled amount of charge through the c-NiSe₂ cathode.

[0035] FIG. 26: The impact of Fe²⁺ concentration on the glycerol valorization in the cathodic half-cell after passing a controlled amount of charge (14.6 C, 29.2 C, or 43.9 C) through the c-NiSe₂ cathode (~1.06 $mg_{Ni} cm^{-2}_{geo}$, ~1 cm^{-2}_{geo}) at 0.60 V vs. RHE in 4 mL of O₂-saturated 0.1 M NaHSO₄/Na₂SO₄ solution (pH~2.8, stirred at 1200 rpm) containing ~50 mM glycerol and various concentration of Fe²⁺ (0.1, 0.5, 1.0, or 2.5 mM). Aqueous phase organic (C₃, C₂, and C₁) product selectivity, glycerol conversion percentage, and carbon balance of all detected aqueous phase organic products were determined by ¹H NMR analyses. As high concentrations of paramagnetic Fe²⁺ ions could cause ¹H NMR peak broadening, the NMR samples were prepared differently depending on the [Fe²⁺] in the aqueous catholyte. When [Fe²⁺] was low (0.1 mM or 0.5 mM), the NMR sample was made by mixing 25 μL of D₂O (containing the maleic acid internal standard) with 475 μL of aqueous catholyte, and the final concentration of the maleic acid internal standard after mixing was ~5 mM. When [Fe²⁺] was high (1.0 mM or 2.5 mM), the NMR sample was made by mixing 450 μL of D₂O (containing the maleic acid internal standard) with 50 μL of aqueous catholyte, and the final concentration of the maleic acid internal standard after mixing is ~0.5 mM.

[0036] FIG. 27: Panel (a) shows Raman spectra and panel (b) shows X-ray photoelectron spectra of c-NiSe₂/CFP before and after half-cell studies of the cathodic valorization of glycerol via the electro-Fenton process at 0.60 V vs. RHE in O₂-saturated 0.1 M NaHSO₄/Na₂SO₄ (pH~2.8) containing ~50 mM glycerol and 0.5 mM Fe²⁺.

[0037] FIG. 28: Panel (a) shows a schematic of the two-compartment three-electrode setup for half-cell studies of the direct anodic oxidation of glycerol at Pt/C anode. Panel (b) shows cyclic voltammograms of Pt/C anode (2 $mg_{Pt} cm^{-2}_{geo}$, 1 cm^{-2}_{geo}) for glycerol oxidation. Panel (c) shows chronopotentiometry curves when passing a controlled amount of charge (14.8 C, 29.7 C, or 45.1 C) through the Pt/C anode at 1.7 mA in 4 mL of Ar-saturated 0.05 M H₂SO₄

solution (pH~1.2, stirred at 1200 rpm) containing ~50 mM glycerol. Panel (d) shows ^1H NMR spectra before and after passing a controlled amount of charge through the Pt/C anode. Each NMR sample in (d) was made by mixing 25 μL of D_2O (containing the maleic acid internal standard) with 475 μL of aqueous anolyte, and the final concentration of the maleic acid internal standard after mixing was ~5 mM. As the amount of passed charge increased, the solution volume in the anode compartment decreased due to evaporation under the Ar gas flow. Panel (e) shows aqueous phase organic (C_3 , C_2 , and C_1) product selectivity, glycerol conversion percentage, and carbon balance of all detected aqueous phase organic products determined by ^1H NMR results after passing a controlled amount of charge through the Pt/C anode.

[0038] FIG. 29: Shows a schematic of the two-compartment three-electrode setup for linear paired electrochemical valorization of glycerol at c-NiSe₂ cathode and Pt/C anode. The electro-Fenton process for glycerol valorization takes place in the cathode compartment at the c-NiSe₂ cathode in O₂-saturated NaHSO₄/Na₂SO₄ buffer solution (pH~2.8) containing ~50 mM glycerol and 0.5 mM Fe²⁺. The direct anodic oxidation of glycerol takes place in the anode compartment at the Pt/C anode in Ar-saturated H₂SO₄ solution containing ~50 mM glycerol. Protons are transported through the Nafion 117 membrane to stabilize the acidic pH of the cathode compartment.

[0039] FIG. 30: The c-NiSe₂ cathode potential and the Pt/C anode potential during the linear paired electrochemical valorization of glycerol (catholyte: O₂-saturated NaHSO₄/Na₂SO₄ solution containing ~50 mM glycerol and 0.5 mM Fe²⁺, pH~2.8; anolyte: Ar-saturated H₂SO₄ solution containing ~50 mM glycerol) under supporting electrolyte condition I (shown in panel A: 0.1 M NaHSO₄/Na₂SO₄ for catholyte, 0.05 M H₂SO₄ for anolyte) or condition II (shown in panel B: 0.5 M NaHSO₄/Na₂SO₄ for catholyte, 0.5 M H₂SO₄ for anolyte).

[0040] FIG. 31: Computational pre-screening of stability, selectivity, and activity of metal compound-based 2e⁻ ORR catalysts. Panel (a) shows crystal structures of pyrite- and marcasite-type metal chalcogenides. Panel (b) shows energetics of O* and OH* adsorption to their preferential binding sites on the most stable facets of c-CoS₂, c-CoSe₂, o-CoSe₂, and c-NiSe₂. Panel (c) shows comparisons of free energies of different O* and/or OH* coverages on c-NiSe₂ (100) surface unit cell including two Ni and four Se sites. For 3 O* and 4 O* coverages, two O* bind to Ni, and the rest of O* bind to Se. For the other O* and/or OH* coverages, all adsorbates bind to Ni. (d) Free energy diagrams of the 2e⁻ and 4e⁻ ORR pathways.

[0041] FIG. 32: Structural characterization of as-synthesized PdSe₂. Panel (a) shows crystal structure of PdSe₂ viewed down the [200] and [002] directions. Panel (b) shows powder x-ray diffraction pattern of PdSe₂ compared to the standard pattern. Panel (c) shows SEM micrograph of PdSe₂ with overlaid SEM-EDS atomic ratios. Panel (d) shows Raman spectrum of PdSe₂ with previously calculated Raman modes overlaid. Panel (e) shows Pd L₃ edge XANES of PdSe₂ with Pd foil, PdO, and K₂PdCl₆ shown as oxidation state standards.

[0042] FIG. 33: Rotating ring disk electrode (RRDE) results of PdSe₂. Panel (a) shows PdSe₂ measured in O₂-saturated conditions in 0.05 M NaPi buffer (pH=6.5) and 0.05 H₂SO₄ (pH=1.2), and panel (b) shows with a kinetic current

comparison plot of PdSe₂ in neutral conditions compared to other 2e⁻ ORR catalysts measured in neutral conditions from the literature, and panel (c) shows extended stability plot of PdSe₂ measured at a constant potential of 0 V vs. RHE for >6 hours (dashed lines indicate ring cleaning via CV).

[0043] FIG. 34: Bulk electrolysis of PdSe₂ (compared to o-CoSe₂) measured in 0.5 M NaPi buffer. Panel (a) shows current comparison, panel (b) shows concentration of H₂O₂, panel (c) shows total accumulation of H₂O₂, and panel (d) shows H₂O₂ selectivity over time.

[0044] FIG. 35: Evaluation of the stability of PdSe₂. Panel (a) shows leached Pd and Se measured by ICP-OES after electrolysis at 0.2 V vs. RHE and 0.3 V vs. RHE, panel (b) shows Raman spectra, panel (c) shows XRD and panel (d) shows XPS Se 2d peak of PdSe₂/CFP after 6 hours of ORR operation at the labeled potentials compared to the pristine sample, and panel (e) shows operando XANES and panel (f) shows EXAFS at E_{oc} (the open circuit potential) and at several applied potentials as labeled.

[0045] FIG. 36: Surface Pourbaix diagrams of the (001) and (100) surfaces of PdSe₂. Each line represents the free energy of formation of each configuration. The clean surface, H₂O(l) and H⁺/e⁻ are used as reference states.

[0046] FIG. 37: Calculated free energy diagrams of 2e⁻ ORR pathways and their competing steps on the (001) and (100) PdSe₂ at the calculated equilibrium potential.

[0047] FIG. 38: The interaction of OOH* with the external electric field on PdSe₂. X-axis is electric field in V/Å and y-axis is the interaction in eV.

[0048] FIG. 39: Electrosynthesis of H₂O₂ in a flow cell on a PdSe₂/GDE electrode. A constant current of -30 mA (~5 mA cm⁻²), -60 mA (~10 mA cm⁻²), and -85 mA (~15 mA cm⁻²) in a buffer solution of 0.25 M Na₂HPO₄/0.25 M NaH₂PO₄ (initial pH~6.5). Panel (a) shows schematic of the 3-layer GDE/flow-cell assembly with each layer annotated and a representative SEM image of the PdSe₂ catalyst dispersed on GDE electrode. Panel (b) shows cyclic voltammogram of the PdSe₂ loaded GDE before the electrosynthesis process, panel (c) shows potential vs. time curve (continuous line, left-axis) and Faradaic efficiency (dots, right axis) of the PdSe₂/GDE during constant current electrosynthesis, and panel (d) shows the corresponding H₂O₂ accumulation during the H₂O₂ electrosynthesis processes.

[0049] FIG. 40: Long term stability of PdSe₂. Panel (a) shows CV of PdSe₂/GDE electrode with high Nafion loading in the catalyst dispersion (~0.05 mg, or 1 mL of 5 wt. % solution), and panel (b) shows galvanostatic test of PdSe₂ over 48 hours at -75 mA, stopped due to counter electrode overload.

DETAILED DESCRIPTION OF THE INVENTION

[0050] Disclosed herein is an electrochemical cell and a method of using the same. The present technology allows for harnessing electricity (which could be generated from solar and wind) for electrochemical synthesis of H₂O₂ and high-value chemicals from biomass feedstocks, which offers a sustainable alternative to conventional centralized chemical manufacturing. For example, glycerol is a byproduct of biodiesel production and has become a surplus biomass-derived chemical. Oxidative upgrading of glycerol is very attractive, because all C₃ and C₂ oxidation products have higher economic values than glycerol. Compared to thermal

oxidation that requires high temperature and oxygen pressure, electrochemical oxidation poses several advantages including near-ambient operation, less reagent waste, and distributed small-scale production.

[0051] Electrochemical oxidation of glycerol typically occurs at catalytic anodes made of noble metals or earth-abundant electrocatalysts, which is paired with either four-electron oxygen reduction reaction ($4e^-$ ORR) in a galvanic cell or hydrogen evolution reaction (HER) in an electrolytic cell (FIG. 1). In either case, the chemicals generated at cathode have lower economic values (e.g., H_2 from steam methane reforming) than the glycerol-derived chemicals generated at anode [e.g., dihydroxyacetone (DHA)]. Anodic glycerol oxidation has been paired with CO_2 or CO reduction reaction (CO_2 /CORR) that generates C_1 and/or C_{2+} products at the cathode, but the different cathode and anode feeds lead to different product portfolios between the two half-cells with additional system complexity and separation cost. Using glycerol as the sole feed in a so-called linear paired electrochemical process allows for production of value-added oxidation products at both cathode and anode simultaneously could be appealing.

[0052] An electrochemical cell is defined as a device that may produce an electrical current from a chemical reaction and/or use electrical energy to drive a chemical reaction. The electrochemical cell here includes a cathode immersed in an electrolyte and an anode immersed in an acidic electrolyte. In some embodiments of the disclosed technology, the electrochemical cell may contain two or three electrodes. The two-electrode configuration may contain a working electrode and a counter electrode. The three-electrode configuration may contain a working electrode, a reference electrode, and a counter electrode.

[0053] In one aspect, the electrochemical cell includes an electrolyte. An electrolyte is defined as a substance that conducts electric current. The catholyte is defined as an electrolyte used in the cathodic compartment of the electrochemical cell. An anolyte is defined as an electrolyte used in the anodic compartment of the electrochemical cell. The electrolyte, catholyte, and anolyte may be the same material or different material.

[0054] In one aspect of the technology, the electrochemical cell contains a cathode with an electrocatalyst that can perform the two-electron oxygen reduction reaction ($2e^-$ ORR). The oxygen reduction reaction (ORR) is the reduction half-reaction whereby oxygen is reduced to water via the four-electron pathway or hydrogen peroxide via the two-electron pathway. Hydrogen peroxide (H_2O_2) is a useful oxidant for a range of applications including the pulp and paper industry, chemical manufacturing, wastewater treatment, healthcare disinfection, and biomass valorization. Other chemical methods of hydrogen peroxide production, including via the anthraquinone process, are energy-intensive and unsafe as it produces concentrated H_2O_2 at centralized plants and requires hazardous transportation to end-users. Alternatively, decentralized electrosynthesis of H_2O_2 via $2e^-$ ORR offers a more sustainable route because it can be driven by increasingly affordable renewable electricity, eliminate the need for H_2 gas, and produce dilute H_2O_2 directly at the point of use, which is advantageous for distributed applications. A key challenge is to develop robust electrocatalysts with high activity, selectivity, and stability for the desired $2e^-$ (vs. the competing $4e^-$) ORR pathway.

[0055] The thermodynamics of $2e^-$ ORR ($O_2+2 H^++2 e^- \rightarrow H_2O_2$, standard equilibrium potential $E^\circ=0.69$ V vs. reversible hydrogen electrode, RHE) and $4e^-$ ORR ($O_2+4 H^++4e^- \rightarrow 2 H_2O$, $E^\circ=1.23$ V vs. RHE) are often described by the volcano relations between the thermodynamic limiting potential (UL) and the energetics of key reaction intermediates. $2e^-$ ORR proceeds via the adsorption of OOH^* ($O_2+*+H^++e^- \rightarrow OOH^*$, where $*$ is an unoccupied surface binding site) followed by its desorption to form H_2O_2 ($OOH^*+H^++e^- \rightarrow H_2O_2+*$); $4e^-$ ORR occurs via the O—O bond cleavage processes (thermal cleavage: $O_2+2* \rightarrow 2 O^*$, and $OOH^*+* \rightarrow O^*+OH^*$; electrochemical reductive elimination: $OOH^*+H^++e^- \rightarrow O^*+H_2O$). The key intermediates of $2e^-$ ORR (OOH^*) and $4e^-$ ORR (OH^*) follow a linear scaling relationship (typically $\Delta G_{OOH^*} = \Delta G_{OH^*} + 3.2$ eV), resulting in the $2e^-$ and $4e^-$ ORR volcanos. The $2e^-$ ORR activity, determined by the OOH^* adsorption energy (ΔG_{OOH^*}), is maximized at the peak of $2e^-$ ORR volcano. Moving leftwards from $2e^-$ ORR volcano peak, the catalyst surface binds OOH^* (and OH^*) more strongly, and UL of $4e^-$ ORR is always more positive than that of $2e^-$ ORR, indicating the $4e^-$ pathway will dominate because there is a greater driving force to form H_2O than H_2O_2 . To the right of $2e^-$ ORR volcano peak, UL of the $2e^-$ and $4e^-$ pathways overlap and moving rightwards will increase the selectivity (but lowering the activity) for $2e^-$ ORR because the formation of OH^* (and OOH^*) becomes more difficult. Besides electronic effects described above, the $2e^-$ ORR selectivity can also be improved by controlling geometric (or ensemble) effects by rearranging catalyst surface atoms to change adsorption sites of reaction intermediates, so that O^* can be destabilized relative to OOH^* , deviating from the conventional scaling relationship.

[0056] Several classes of selective $2e^-$ ORR catalysts, including noble metal alloys, carbon nanomaterials, single-atom catalysts, and metal compounds, have been studied for H_2O_2 electrosynthesis under different pH conditions. Among these reports, $2e^-$ ORR catalysts in alkaline solution have been mostly extensively studied, but H_2O_2 is unstable in alkaline solution. In contrast, the less studied acidic and neutral conditions are attractive for several reasons besides the chemical stability of H_2O_2 . Acidic H_2O_2 electrosynthesis can proceed in the technologically mature proton exchange membrane (PEM) devices. On-site water disinfection and environmental treatment can also benefit from acidic H_2O_2 electrosynthesis because the electro-Fenton process operates at the optimum pH of about 3 to convert the produced H_2O_2 into the more oxidizing hydroxyl radical ($\cdot OH$) for the removal of persistent bacteria and organic pollutants. For direct applications, neutral solutions can avoid the need for neutralization. However, high-performance yet cost-effective $2e^-$ ORR electrocatalysts in acidic and neutral solutions are still being developed.

[0057] One class of selective $2e^-$ ORR electrocatalysts are metal chalcogenides. In one embodiment of the disclosed technology, the cathode includes an electrocatalyst composed of a metal chalcogenide. A chalcogenide is defined as a chemical compound with at least one chalcogen anion (any anionic form of elements in Group 16 of the periodic table) and at least one more electropositive element. In one embodiment, the chalcogen anion may be a sulfide, selenide, telluride, polonide, or, less commonly, oxide, or any combination thereof.

[0058] In one embodiment the electropositive element of the metal chalcogenide is at least one metal. In one embodiment the metal may be earth-abundant or noble metals, including transition metals, post-transition metals, or any combination thereof. In some embodiments, the metal may be Li, Be, Na, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Cs, Ba, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, Fr, Ra. In some embodiments the metal chalcogenide may be cubic pyrite-type $c\text{-CoS}_2$, $c\text{-CoSe}_2$, $c\text{-NiSe}_2$, orthorhombic marcasite-type $o\text{-CoS}_2$, layered PdSe_2 , layered MoSe_2 , MoS_2 , MoSe_2 , WS_2 , WSe_2 , or any combination thereof. In other embodiments, the metal chalcogenide is a spinel such as $\text{CuCO}_{2-x}\text{Ni}_x\text{S}_4$.

[0059] Another aspect of $2e^-$ ORR metal chalcogenide electrocatalysts is the preferential binding of O^* and OH^* products to either the chalcogenide or the metal. Previously studied metal chalcogenide electrocatalysts, including CoS_2 and CoSe_2 , demonstrate preferential binding of O^* and OH^* to the sulfide and selenide. This has implications for electrocatalyst stability. Surface oxidation is more likely in electrocatalysts where O^* and OH^* more strongly bind to the chalcogenide due to the formation of highly soluble anions, such as SO_4^{2-} , and is followed by metal leaching and electrocatalyst degradation. One embodiment of the disclosed technology includes the preferential binding of O^* and OH^* to the earth abundant metal of the metal chalcogenide. In one embodiment, the electrocatalyst demonstrates preferential binding of O^* and OH^* to Ni.

[0060] In another aspect of the disclosed technology, the electrochemical cell may additionally contain reagents for electrosynthesis purposes. Generally, this involves reagents needed to generate hydroxyl radicals ($\cdot\text{OH}$) via the advanced oxidation processes, including hydrogen peroxide (H_2O_2), and a regenerable metal ion. In one embodiment, the advanced oxidation may be via the electro-Fenton process, wherein the regenerable metal ion is Fe^{2+} . In other embodiments, the advanced oxidation may be via a Fenton-like process wherein the regenerable metal ion is Co, Cu, or Mn. In some embodiments a regenerable metal ion is not required for the production of the hydroxyl radical. For reasons discussed above, the pH of the electrochemical cell is acidic. In some embodiments, the electrochemical cell has a pH no lower than 0 and no higher than 7. In one embodiment, the electrochemical cell has a pH no lower than 0 and no higher than 4. In another embodiment, the electrochemical cell has a pH between 4.0 and 7.0. In one embodiment where the regenerable metal ion is Fe^{2+} , the electrochemical cell has a pH no lower than 0 and no higher than 4. In some embodiments the pH of the electrochemical cell is adjusted by the addition of a mineral acid. In some embodiments the mineral acid is sulfuric acid, hydrochloric acid, or perchloric acid. In one embodiment where the regenerable metal ion is Fe^{2+} , the pH of the electrochemical cell may be about 3 to prevent the precipitation of iron oxides in more basic conditions. Other regenerable metals may have other ideal acidic, basic, or neutral conditions of the electrochemical cell.

[0061] In one embodiment, the electrochemical cell electrolyte further includes a biomass-derived feedstock. Biomass-derived feedstock is defined as sustainable feedstock derived from biomass for chemicals and energy products. In some embodiments, biomass-derived feedstock includes forest product wastes, agricultural residues, organic fractions of

municipal solid wastes, paper, cardboard, plastic, food waste, green waste, and other waste. In other embodiments, the biomass-derived feedstock may be polyols such as glycerol, hydroxymethylfurfural (HMF), glucose, fructose, and other monosaccharide and disaccharide (sugar) molecules, lignin, hemicellulose, cellulose, or other oxygen-containing compounds including compounds with ether, alcohol, aldehyde, and ester functional groups.

[0062] In some embodiments, the oxidation products of the electrochemical half cell starting from glycerol include C_3 , C_2 , and C_1 products. In some embodiments the oxidation products include aldehyde and ketone functional groups. In some embodiments the oxidation product may include dihydroxyacetone (DHA), glyceraldehyde (GLAD), glyceric acid (GLA), hydroxypyruvic acid (HPA), glycolaldehyde (GAD), glycolic acid (GA), glyoxylic acid (GLOA), formic acid (FA), or any combination thereof.

[0063] Advanced oxidation products are typically only produced at one electrode of the electrochemical cell. In one embodiment, the anode produces oxidation products. One aspect of the disclosed technology is an electrochemical cell wherein electrochemical reactions at both the cathode and anode both produce oxidation products, sometimes referred to as linear paired electrochemical cell.

[0064] In another aspect of the technology, the electrochemical cell may contain one or more compartments. In one embodiment, the electrochemical cell is oriented in a two-compartment H-type electrochemical cell (denoted as H-cell), wherein the two compartments are separated by a proton-permeable membrane. In another embodiment, electrochemical flow cell configurations may be used. In electrochemical flow cells, liquid biomass-derived feedstocks, reagents, and electrolytes may be continuously or periodically flowed past electrodes. In one embodiment, the proton permeable membrane may be a Nafion, Fumasep, Fumapem, or Aquivion membrane. In one embodiment the cathode is isolated to one compartment and the anode is isolated to the second compartment. %

[0065] In one embodiment, the anode may include platinum, palladium, ruthenium, antimony, bismuth, tin, and bimetallic alloys of these metals, ruthenium oxide, iridium oxide, or boron doped diamond.

[0066] In one embodiment the biomass-derived feedstock could be the same in each of the electrochemical cell compartments, representing the linear paired electrochemical process starting with the same feedstock. In another embodiment the biomass-derived feedstock in the cathodic compartment may be different from the biomass-derived feedstock in the anodic compartment, representing the paired electrochemical process in general.

[0067] The anodic and cathodic reaction products may be mixed and further purified together but they need not be. Where the anodic and cathodic reaction products are expected to be similar, mixing and purifying the reaction products from both the anodic and cathodic reactions together may simplify processing or reduced costs. In some embodiments, where biomass-derived feedstock is the same in each of the electrochemical cell compartments for the linear paired electrochemical process, the anodic and cathodic reaction products may be mixed and further purified together.

[0068] A further aspect of the disclosed technology is a method of preparing oxidation product of biomass-derived feedstock. In one embodiment of the method, the applied

potential to the anode is between 0.00 and 1.50 V vs. RHE. In another embodiment, the applied potential to the cathode is between 0.00 and 0.70 V vs. RHE.

[0069] Another aspect of the disclosed technology is a method of preparing oxidation product of biomass-derived feedstock with externally applied bias to the two-compartment H-cell. In one embodiment the externally applied bias is less than 0.01 V, 0.02V, 0.03 V, 0.04V, 0.05 V, 0.06 V, 0.07 V, 0.08 V, 0.09 V, 0.10 V, 0.11 V, 0.12 V, 0.13 V, 0.14 V, 0.15 V, 0.16 V, 0.17 V, 0.18 V, 0.19 V, 0.20 V, 0.21 V, 0.22 V, 0.23 V, 0.24 V, 0.25 V, 0.26 V, 0.27 V, 0.28 V, 0.29 V, 0.30 V, 0.31 V, 0.32 V, 0.33 V, 0.34 V, 0.35 V, 0.36 V, 0.37 V, 0.38 V, 0.39 V, 0.40 V, 0.41 V, 0.42 V, 0.43 V, 0.44 V, 0.45 V, 0.46 V, 0.47 V, 0.48 V, 0.49 V, 0.50 V, 0.51 V, 0.52 V, 0.53 V, 0.54 V, 0.55 V, 0.56 V, 0.57 V, 0.58 V, 0.59 V, 0.60 V, 0.61 V, 0.62 V, 0.63 V, 0.64 V, 0.65 V, 0.66 V, 0.67 V, 0.68 V, 0.69 V, 0.70 V, 0.71 V, 0.72 V, 0.73 V, 0.74 V, 0.75 V, 0.76 V, 0.77 V, 0.78 V, 0.79V, 0.80V, 0.81 V, 0.82 V, 0.83 V, 0.84 V, 0.85 V, 0.86 V, 0.87 V, 0.88 V, 0.89 V, 0.90 V, 0.91 V, 0.92 V, 0.93 V, 0.94 V, 0.95 V, 0.96 V, 0.97 V, 0.98 V, 0.99 V, 1.00 V, 1.01 V, 1.02V, 1.03 V, 1.04V, 1.05 V, 1.06 V, 1.07 V, 1.08 V, 1.09 V, 1.10 V, 1.11 V, 1.12 V, 1.13 V, 1.14 V, 1.15 V, 1.16 V, 1.17 V, 1.18 V, 1.19 V, 1.20 V, 1.21 V, 1.22 V, 1.23 V, 1.24 V, 1.25 V, 1.26 V, 1.27 V, 1.28 V, 1.29 V, 1.30 V, 1.31 V, 1.32 V, 1.33 V, 1.34 V, 1.35 V, 1.36 V, 1.37 V, 1.38 V, 1.39 V, 1.40 V, 1.41 V, 1.42 V, 1.43 V, 1.44 V, 1.45 V, 1.46 V, 1.47 V, 1.48 V, 1.49 V, or 1.50 V.

[0070] By way of example, glycerol valorization in the cathodic half-cell via the electro-Fenton process was studied by applying a fixed potential of 0.60 V vs. RHE to c-NiSe₂ grown on carbon fiber paper (denoted as c-NiSe₂/CFP) cathode (~1.06 mg_{Ni} cm⁻²_{geo}, ~1 cm⁻²_{geo}) in O₂-saturated 0.1 M NaHSO₄/Na₂SO₄ (pH~2.8) containing ~50 mM glycerol and 0.5 mM Fe²⁺, and the cathode current was ~1.7 mA. Direct oxidation of glycerol in the anodic half-cell was studied by applying a fixed current of 1.7 mA to nanoparticulate Pt supported on carbon black (denoted as Pt/C) anode (2 mg_{Pt} cm⁻²_{geo}, 1 cm⁻²_{geo}) in Ar-saturated 0.05 M H₂SO₄ (pH~1.2) containing ~50 mM glycerol, and the anode potential was ~0.55 V vs. RHE at pH~1.2. If c-NiSe₂/CFP cathode (in O₂-saturated 0.1 M NaHSO₄/Na₂SO₄ containing ~50 mM glycerol and 0.5 mM Fe²⁺, pH~2.8) and Pt/C anode (in Ar-saturated 0.05 M H₂SO₄ containing ~50 mM glycerol, pH~1.2) were coupled together and both operated at 1.7 mA for glycerol valorization in a linear paired electrochemical system (as shown in FIG. 29), the cell potential (E_{cell}) in principle can be estimated by the cathode potential (E_{cathode}) and the anode potential (E_{anode}) from the respective half-cell studies. From the cathodic half-cell study:

[0071] E_{cathode} (at ~1.7 mA)=0.60 V vs. RHE (at pH~2.8)~0.435 V vs. standard hydrogen electrode (SHE)

From the anodic half-cell study:

[0072] E_{anode} (at 1.7 mA)~0.55 V vs. RHE (at pH~1.2)~0.479 V vs. SHE

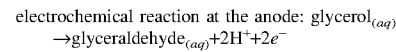
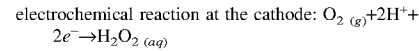
[0073] Under the ideal assumption of no internal resistance (i.e., no ohmic overpotential) in the linear paired electrochemical system:

$$\begin{aligned} E_{cell}(\text{at } \sim 1.7 \text{ mA}) &= E_{cathode} \text{ vs. SHE} - E_{anode} \text{ vs. SHE} \\ &= \sim (0.435 - 0.479) \text{ V} \\ &= \sim -0.044 \text{ V} \end{aligned}$$

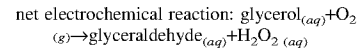
[0074] This example shows that to deliver a current of ~1.7 mA for glycerol valorization at both c-NiSe₂/CFP cathode and Pt/C anode, the linear paired electrochemical system ideally can operate as an electrolytic cell at an external bias as low as <0.05 V with almost no external energy input needed if the internal resistance is negligible.

[0075] The thermodynamic basis of the linear paired glycerol valorization process is provided. Intuitively, the overall process is a controlled partial oxidation of glycerol by oxygen gas to produce mainly C₃ and C₂ oxidation products in an electrochemical cell, and such oxidation process should be thermodynamically spontaneous.

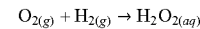
[0076] Considering an ideally simplified linear paired process where both the electro-Fenton process and the direct anodic oxidation process generate a single oxidation product of glyceraldehyde from glycerol, the respective electrochemical reactions at the cathode and the anode should be:



The balanced net electrochemical reaction that determines the overall achievable cell potential of this simplified linear paired glycerol-to-glyceraldehyde valorization process should be:



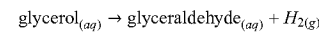
Because the standard Gibbs free energies of formation ($\Delta_f G^\circ$) of these organic compounds are not directly available, we consider the net electrochemical reaction as the combination of the following two reactions:



$$\Delta G^\circ = \Delta G_f^\circ[\text{H}_2\text{O}_{2(g)}] + \Delta G_{solv}^\circ[\text{H}_2\text{O}_{2(g)}] = \Delta G_f^\circ[\text{H}_2\text{O}_{2(g)}] - R \cdot T \cdot \ln(k_H)$$

$$= -105.6 \frac{\text{kJ}}{\text{mol}} \times 1 \text{ mol} - 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times 298 \text{ K} \times$$

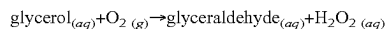
$$\ln\left(99000 \frac{\text{mol}}{\text{kg} \cdot \text{bar}}\right) \times 1 \text{ mol} = -134.1 \text{ kJ}$$



$$\Delta G^\circ = 9.4 \text{ kcal mol}^{-1} \times 4.184 \text{ kJ kcal}^{-1} \times 1 \text{ mol} = 39.3 \text{ kJ}$$

where $\Delta G_f^\circ[\text{H}_2\text{O}_{2(g)}]$ may be sourced from a reference, such as the CRC Handbook of Chemistry and Physics, $\Delta G_{solv}^\circ[\text{H}_2\text{O}_{2(g)}]$ is the solvation free energy of H₂O_{2(g)} based on the experimental Henry's law constant (k_H), and ΔG° for glycerol_(aq)→glyceraldehyde_(aq)+H_{2(g)} may be sourced from a theoretical report and may be calculated with quantum chemistry software, such as the Gaussian 03 program, and includes both electrostatic and nonelectrostatic components of the solvation free energies.

[0077] As a result, the net electrochemical reaction is thermodynamically spontaneous and results in a galvanic cell with an overall achievable cell potential of 0.49 V:

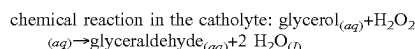


$$\Delta G^\circ = -134.1 \text{ kJ} + 39.3 \text{ kJ} = -94.8 \text{ kJ}$$

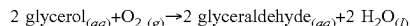
$$\Delta G^\circ / (-n \times F) = -94.8 \text{ kJ} / (-2 \text{ mol} \times 96485 \text{ C mol}^{-1}) = 0.49 \text{ V}$$

where n is the number of electrons transferred, and F is the Faraday constant.

The linear paired glycerol valorization process is a hybrid of electrochemical and chemical steps. Besides the as-mentioned electrochemical reactions at the cathode and the anode, chemical reaction of glycerol oxidation using H_2O_2 as the oxygen source takes place in the catholyte solution:



The ΔG° ($=-300.8 \text{ kJ}$) of this chemical reaction in the catholyte solution cannot be harnessed electrochemically, and thus the overall achievable cell potential for the linear paired glycerol valorization process is governed by the $\text{O}_2/\text{H}_2\text{O}_2$ redox couple but not the $\text{O}_2/\text{H}_2\text{O}$ redox couple. Combining all steps together, the overall cell reaction of this simplified linear paired glycerol-to-glyceraldehyde valorization process should be:



[0078] This overall cell reaction is thermodynamically spontaneous ($\Delta G^\circ = -395.6 \text{ kJ}$), but only part of the ΔG° is harnessed electrochemically to result in a galvanic cell with an overall achievable cell potential of 0.49 V (as discussed above).

[0079] Similarly, it holds true for other oxidation products (dihydroxyacetone, glyceric acid, etc.) that the linear paired glycerol valorization process results in a galvanic cell that is thermodynamically spontaneous, which can be derived from the calculated thermochemical data found in ref.

[0080] Earlier in this description we estimated based on experimental half-cell studies that, to deliver a current of $\sim 1.7 \text{ mA}$, our linear paired electrochemical system for glycerol valorization ideally can operate as an electrolytic cell at an external bias as low as $< 0.05 \text{ V}$ if the internal resistance is negligible. In this estimate, the linear paired electrochemical system operates as an electrolytic cell rather than a galvanic cell, because both $2e^-$ ORR at the NiSe_2 cathode and glycerol oxidation at the Pt anode require kinetic overpotentials to deliver a catalytic current of $\sim 1.7 \text{ mA}$. By designing more active cathode and anode electrocatalysts to further reduce the kinetic overpotentials and further optimizing the electrochemical device design, linear paired electrochemical systems for glycerol valorization that need no external bias and no external energy input could be realized.

[0081] The linear paired system ideally could operate at an external bias as low as $< 0.05 \text{ V}$ if there was no internal resistance. In FIG. 30a, the measured external bias was higher than this estimated ideal value, mostly caused by the large solution IR drop (where IR refers to the product of current and resistance) at the anode as it situated on the opposite side of the $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference electrode across the Nafion 117 membrane. The magnitude of the ohmic overpotential (solution IR drop) at the anode was almost identical to the measured external bias, suggesting that the

ideal estimation in provided above is still valid. The large solution IR drop at the anode was mostly caused by the solution resistance rather than the membrane resistance, because it was almost unaffected by the membrane thickness when the catholyte and anolyte compositions remained the same (see comparisons between the $183 \mu\text{m}$ -thick Nafion 117 membrane and the $89 \mu\text{m}$ -thick Nafion NE1035 membrane in Table 4). As shown in FIG. 30b, by increasing the supporting electrolyte concentrations of both catholyte and anolyte, the measured external bias was reduced because of the decrease in the solution IR drop at the anode. To operate this linear paired system at an even lower (or zero) external bias in the future, the ohmic overpotential needs to be further reduced, and one possible optimization pathway is to employ zero-gap cell designs involving membrane electrode assemblies.

Miscellaneous

[0082] Unless otherwise specified or indicated by context, the terms “a”, “an”, and “the” mean “one or more”. For example, “a molecule” should be interpreted to mean “one or more molecules.”

[0083] As used herein, “about”, “approximately”, “substantially”, and “significantly” will be understood by persons of ordinary skill in the art and will vary to some extent on the context in which they are used. If there are uses of the term which are not clear to persons of ordinary skill in the art given the context in which it is used, “about” and “approximately” will mean plus or minus $\leq 10\%$ of the particular term and “substantially” and “significantly” will mean plus or minus $> 10\%$ of the particular term.

[0084] As used herein, the terms “include” and “including” have the same meaning as the terms “comprise” and “comprising.” The terms “comprise” and “comprising” should be interpreted as being “open” transitional terms that permit the inclusion of additional components further to those components recited in the claims. The terms “consist” and “consisting of” should be interpreted as being “closed” transitional terms that do not permit the inclusion additional components other than the components recited in the claims. The term “consisting essentially of” should be interpreted to be partially closed and allowing the inclusion only of additional components that do not fundamentally alter the nature of the claimed subject matter.

[0085] All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., “such as”) provided herein, is intended merely to better illuminate the invention and does not pose a limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

[0086] All references, including publications, patent applications, and patents, cited herein are hereby incorporated by reference to the same extent as if each reference were individually and specifically indicated to be incorporated by reference and were set forth in its entirety herein.

[0087] Preferred aspects of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Variations of those preferred aspects may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect a person having ordinary skill in the art to employ

such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.

ILLUSTRATIVE EMBODIMENTS

[0088] Embodiment 1: An electrochemical cell including an electrolyte and a cathode immersed in the electrolyte,

[0089] wherein the cathode includes a two-electron oxygen reduction reaction ($2e^-$ ORR)

[0090] electrocatalyst composed of a metal chalcogenide,

[0091] wherein the metal is Ni or Pd.

[0092] Embodiment 2: The electrochemical cell of embodiment 1, wherein the metal is Ni.

[0093] Embodiment 3: The electrochemical cell of embodiment 2, wherein the metal chalcogenide includes c-NiSe₂.

[0094] Embodiment 4: The electrochemical cell of any one of embodiments 1-3, wherein the electrolyte has a pH below 4.0, optionally wherein the electrolyte has a pH between 0.0 and 4.0 pH or any pH therebetween.

[0095] Embodiment 5: The electrochemical cell of embodiment 1, wherein the metal is Pd.

[0096] Embodiment 6: The electrochemical cell of embodiment 5, wherein the metal chalcogenide includes layered PdSe₂.

[0097] Embodiment 7: The electrochemical cell of any one of embodiments 1 or 5-6, wherein the electrolyte has a pH above 4.0, optionally wherein the electrolyte has a pH between 4.0 and 8.0 pH or any pH therebetween.

[0098] Embodiment 8: The electrochemical cell of any one of embodiments 1-7, wherein the electrolyte includes oxygen (O₂), hydrogen peroxide (H₂O₂), hydroxyl radical (\cdot OH), a regenerable metal ion, and a first biomass-derived feedstock.

[0099] Embodiment 9: The electrochemical cell of embodiment 8 further including an acidic anolyte and an anode immersed in the anolyte, wherein the anolyte includes a second biomass-derived feedstock.

[0100] Embodiment 10: A method for production of hydrogen peroxide, the method including introducing oxygen into the electrochemical cell according to any one of embodiments 1-9 under conditions sufficient for preparing the hydrogen peroxide.

[0101] Embodiment 11: The method of embodiment 10, wherein the conditions sufficient for preparing hydrogen peroxide include a potential between 0.00 and 0.70 V vs. RHE applied to the cathode.

[0102] Embodiment 12: An electrochemical cell including an acidic catholyte, a cathode immersed in the catholyte, an acidic anolyte, and an anode immersed in the anolyte,

[0103] wherein the cathode includes a two-electron oxygen reduction reaction ($2e^-$ ORR)

[0104] electrocatalyst having a metal chalcogenide and the catholyte having oxygen (O₂),

[0105] hydrogen peroxide (H₂O₂), hydroxyl radical (\cdot OH), a regenerable metal ion, and a first biomass-

derived feedstock, and wherein the anolyte includes a second biomass-derived feedstock.

[0106] Embodiment 13: The electrochemical cell of embodiment 12, wherein the two-electron oxygen reduction reaction ($2e^-$ ORR) electrocatalyst includes a metal chalcogenide.

[0107] Embodiment 14: The electrochemical cell of embodiment 13, wherein the metal chalcogenide includes c-NiSe₂.

[0108] Embodiment 15: The electrochemical cell of embodiment 13, wherein the metal chalcogenide includes layered PdSe₂.

[0109] Embodiment 16: The electrochemical cell of embodiment 13, wherein the metal chalcogenide includes pyrite or marcasite type CoSe₂, pyrite type CoS₂, or CuCO₃·Ni₃S₄.

[0110] Embodiment 17: The electrochemical cell of embodiment 13, wherein the metal chalcogenide includes an earth-abundant metal or a noble metal.

[0111] Embodiment 18: The electrochemical cell of embodiment 13, wherein the earth abundant metal includes Ni, Co, Fe, Cu, Mn, or any combination thereof.

[0112] Embodiment 19: The electrochemical cell of embodiment 18, wherein the earth abundant metal includes Ni.

[0113] Embodiment 20: The electrochemical cell of embodiment 18, wherein the earth abundant metal includes Co.

[0114] Embodiment 21: The electrochemical cell of embodiment 17, wherein the noble metal includes Pd.

[0115] Embodiment 22: The electrochemical cell of any one of embodiments 12-21, wherein the acidic catholyte and/or the acidic anolyte has a pH between 0.0 and 4.0 pH.

[0116] Embodiment 23: The electrochemical cell of any one of embodiments 12-22, wherein the regenerable metal ion is Fe²⁺.

[0117] Embodiment 24: The electrochemical cell of any one of embodiments 12-23, wherein the electrochemical cell includes a semipermeable barrier between the cathode from the anode.

[0118] Embodiment 25: The electrochemical cell of any one of embodiments 12-24, wherein the first biomass-derived feedstock or the second biomass-derived feedstock includes glycerol.

[0119] Embodiment 26: The electrochemical cell of any one of embodiments 12-25, wherein each of the catholyte and the anolyte further include oxidation products of the first biomass-derived feed stock and the second biomass derived feed stock.

[0120] Embodiment 27: The electrochemical cell of embodiment 26, wherein the oxidation products include dihydroxyacetone (DHA), glyceraldehyde (GLAD), glyceric acid (GLA), hydroxypyruvic acid (HPA), glycolaldehyde (GAD), glycolic acid (GA), glyoxylic acid (GLOA), formic acid (FA), or any combination thereof.

[0121] Embodiment 28: A method for preparing an oxidation product of a biomass-derived feedstock, the method including introducing the biomass-derived feedstock into the electrochemical cell according to any one of embodiments 1-9 under conditions sufficient for preparing the oxidation product.

[0122] Embodiment 29: The method of embodiment 28, wherein a potential is between 0.00 and 0.70 V vs. RHE is applied to the cathode.

[0123] Embodiment 30: The method of any one of embodiments 28-29, wherein the biomass-derived feedstock includes glycerol.

[0124] Embodiment 31: The method of any one of embodiments 28-30, wherein the electrolyte further includes an oxidation product of the biomass-derived feedstock.

[0125] Embodiment 32: The method of embodiment 31, wherein the oxidation product includes dihydroxyacetone (DHA), glyceraldehyde (GLAD), glyceric acid (GLA), hydroxypyruvic acid (HPA), glycolaldehyde (GAD), glycolic acid (GA), glyoxylic acid (GLOA), formic acid (FA), or any combination thereof.

[0126] Embodiment 33: A method for preparing an oxidation product of a biomass-derived feedstock, the method including introducing the biomass-derived feedstock into the electrochemical cell according to any one of embodiments 12-24 under conditions sufficient for preparing the oxidation product.

[0127] Embodiment 34: The method of embodiment 33, wherein less than 1.0 V of externally applied bias is applied.

[0128] Embodiment 35: The method of embodiment 33, wherein less than 0.2 V of externally applied bias is applied.

[0129] Embodiment 36: The method of any one of embodiments 33-35, wherein the biomass-derived feedstock includes glycerol.

[0130] Embodiment 37: The method of any one of embodiments 33-36, wherein the electrolyte further includes an oxidation product of the biomass-derived feedstock.

[0131] Embodiment 38: The method of embodiment 37, wherein the oxidation product includes dihydroxyacetone (DHA), glyceraldehyde (GLAD), glyceric acid (GLA), hydroxypyruvic acid (HPA), glycolaldehyde (GAD), glycolic acid (GA), glyoxylic acid (GLOA), formic acid (FA), or any combination thereof.

EXAMPLES

Example 1

[0132] Linear paired electrochemical valorization of glycerol requires a cathodic reaction that can generate oxidative species to oxidize glycerol. Hydrogen peroxide (H_2O_2) is an oxidant ($E^\circ=1.76$ V vs. SHE) that can be cathodically generated via the selective $2e^-$ ORR ($\text{O}_2+2\text{H}^++2e^-\rightarrow\text{H}_2\text{O}_2$), and be further converted into the even more oxidizing hydroxyl radical ($\cdot\text{OH}$, $E^\circ=2.80$ V vs. SHE) by the Fe^{2+} -mediated electro-Fenton process in acidic solutions ($\text{Fe}^{2+}+\text{H}_2\text{O}_2+\text{H}^+\rightarrow\text{Fe}^{3+}+\text{H}_2\text{O}+\cdot\text{OH}$) where Fe^{2+} is regenerated at the H_2O_2 -generating cathode ($\text{Fe}^{3+}+e^-\rightarrow\text{Fe}^{2+}$). The application of electro-Fenton process has been largely limited to environmental pollutant removal, but chemically generated $\cdot\text{OH}$ from H_2O_2 has found use in biomass-to-chemical processes such as carbohydrate oxidation and lignin depolymerization.

[0133] Here, we present the cathodic valorization of glycerol via the electro-Fenton process, and the further linear pairing with the anodic oxidation to concurrently produce the same glycerol-derived oxidation products at both cathode and anode (FIG. 1). This is made possible by robust and earth-abundant electrocatalyst, such as NiSe_2 , for the selective $2e^-$ ORR and electro-Fenton process in acidic solutions. Building on the recent developments of transition metal compounds as selective $2e^-$ ORR catalysts that are more

cost-effective than noble metals and more catalytically active than carbon-based materials in acidic solutions, we demonstrate through theory and experiment high selectivity toward acidic $2e^-$ ORR and excellent stability against surface oxidative leaching. Cathodes operated at the optimum potential for H_2O_2 electrosynthesis and electro-Fenton process enables the efficient glycerol oxidation in the cathodic half-cell, with a high glycerol conversion and high selectivity for valuable C_3 products. Finally, a new linear paired electrochemical system having valorization at both the cathode and anode for efficient concurrent glycerol valorization to C_3 products is demonstrated under a marginal external applied bias.

Identifying c- NiSe_2 Catalyst for the Electro-Fenton Process

[0134] The Fe^{2+} -mediated electro-Fenton process operates at an optimum pH of ~ 3 and poses more stringent requirements for catalyst stability than $2e^-$ ORR because OH is more oxidizing than H_2O_2 . Therefore, an electrocatalyst that is not only selective for acidic $2e^-$ ORR but also stable in the presence of strong oxidants such as H_2O_2 and $\cdot\text{OH}$ is needed. We utilized the calculated bulk Pourbaix diagrams available from the Materials Project to identify promising earth-abundant catalyst candidates with high aqueous electrochemical stability in the pH and potential ranges of interest for acidic $2e^-$ ORR. Similar to cubic pyrite-type CoSe_2 (c- CoSe_2 , FIG. 2a), an acidic $2e^-$ ORR catalyst with demonstrated stability, cubic NiSe_2 (c- NiSe_2 , FIG. 2a) exhibits a wide electrochemical stability window in the bulk Pourbaix diagram (FIG. 6). Therefore, NiSe_2 could be a promising cathode catalyst for the electro-Fenton process.

[0135] The promise of c- NiSe_2 as an active and selective $2e^-$ ORR catalyst is revealed by the calculated free energy diagrams of the ORR energetics on the most thermodynamically stable (100) surface. The $2e^-$ ORR (FIG. 2b, solid traces) proceeds via the adsorption of OOH^* ($\text{O}_2(\text{g})+*+\text{H}^++e^-\rightarrow\text{OOH}^*$, where * is the unoccupied surface binding site) followed by its desorption to form H_2O_2 ($\text{OOH}^*+\text{H}^++e^-\rightarrow\text{H}_2\text{O}_2(\text{aq})+*$). At the calculated standard equilibrium potential of $2e^-$ ORR (U_{RHE}°), the preferential binding of OOH^* to the Ni site on c- NiSe_2 is relatively weak (endothermic by 0.10 eV), whereas the Co site on c- CoSe_2 preferentially binds to OOH^* more strongly (exothermic by 0.24 eV). Thus, c- NiSe_2 is expected to be not only active for $2e^-$ ORR as the OOH^* adsorption is nearly thermoneutral at U_{RHE}° , but also selective toward $2e^-$ (vs. $4e^-$) ORR because it is situated on the weak OOH^* binding leg of the $2e^-$ ORR volcano. In contrast, c- CoSe_2 is situated on the strong OOH^* binding leg. Furthermore, the $2e^-$ ORR selectivity is also kinetically governed by the resistance to the O—O bond cleavage in OOH^* , which leads to the competing $4e^-$ ORR (FIG. 2b, dashed traces). We reason that the OOH^* dissociation on pyrite-type structures likely proceeds via a dinuclear pathway across two neighboring metal sites ($\text{OOH}^*+*\rightarrow\text{O}^*+\text{OH}^*$). But this pathway features a high activation barrier of 0.61 eV (0.63 eV) on c- NiSe_2 (c- CoSe_2) and is kinetically disfavored due to the large spacing between the neighboring metal sites separated by diselenide anions. Thus, computational assessments of ORR pathways suggest that c- NiSe_2 should be active and selective for $2e^-$ ORR.

[0136] The surface stability of c-NiSe₂ under aqueous electrochemical environments is evaluated by considering O* and/or OH* adsorbate formation when the surface is in equilibrium with water. Unlike c-CoSe₂ where O* and OH* preferentially bind to Se (Se—O*) and Co (Co—OH*), respectively, Ni on c-NiSe₂ is the preferential binding site for both O* (Ni—O*) and OH* (Ni—OH*). On a surface unit cell including two metal sites and four Se sites, should O* builds up on the c-NiSe₂ surface, a significant O* coverage would have to be reached (which is unlikely because O* binds to Ni endothermically by 0.08 eV at U_{RHE}°) before any O* would bind to Se; however, any presence of O* on c-CoSe₂ would bind to Se immediately (FIG. 2c). Since one possible degradation pathway of pyrite-type structures is the oxidation of dichalcogenide anions followed by the dissolution of metal cations (FIG. 6), the low affinity of O* to Se on c-NiSe₂ suggests an increased resistance to surface oxidation. In addition, OH* binds to Ni more weakly (endothermic by 0.27 eV) than to Co (exothermic by 0.08 eV) at U_{RHE}° , which allows the c-NiSe₂ surface to stay clean and mostly free of adsorbate over a wider range of potentials compared to the c-CoSe₂ surface (FIG. 2c). Note that O* and OH* can also form during ORR if the O—O bond cleavage occurs (FIG. 2b). Therefore, these surface adsorbate analyses suggest c-NiSe₂ should be more resistant to surface oxidation and degradation under aqueous environments and ORR operating conditions. Electrochemical Properties and Stability of c-NiSe₂ for Acidic 2e⁻ ORR

[0137] We synthesized nanostructured c-NiSe₂ (FIG. 7) via a hydrothermal method, and examined the acidic 2e⁻ ORR catalytic properties of the powder sample by drop-casting on a rotating ring-disk electrode (RRDE). We also synthesized nanostructured c-CoSe₂ catalyst as a comparison (FIG. 8). RRDE experiments were performed with various catalyst loadings that resulted in similar ranges of double-layer capacitances (C_{dl}) between these two catalysts (FIG. 9) for fair comparisons. In O₂-saturated 0.05 M H₂SO₄ (pH~1.2), c-NiSe₂ exhibits high H₂O₂ selectivity (up to 95%) and relatively little dependence on overpotential and catalyst loading (FIGS. 3a and 3b). In contrast, although

c-CoSe₂ is more catalytically active toward 2e⁻ ORR, the H₂O₂ selectivity decreases more dramatically with increasing overpotential and catalyst loading (FIGS. 3a and 3b). Such differences between the H₂O₂ selectivity profiles of c-NiSe₂ and c-CoSe₂ are also observed at pH~2.8 in O₂-saturated 0.1 M NaHSO₄/Na₂SO₄ buffer (FIGS. 10 and 11), further showing that c-NiSe₂ is more selective toward acidic 2e⁻ ORR than c-CoSe₂.

[0138] The stability of c-NiSe₂ (vs. c-CoSe₂) catalyst for acidic 2e⁻ ORR was evaluated by long-term RRDE stability tests at various catalyst loadings. The catalyst stability is monitored by tracking the disk potential at a certain disk current density (j_{disk}) or peroxide current density ($j_{peroxide}$) (FIG. 12). The stable disk potential throughout the tests shows that c-NiSe₂ exhibits a higher catalyst stability than c-CoSe₂ at both pH~1.2 (0.05 M H₂SO₄) and pH~2.8 (0.1 M NaHSO₄/Na₂SO₄) (FIGS. 13 and 14). The spent catalysts show no obvious structural and compositional change (FIG. 15). We further performed elemental analyses of the spent electrolytes to quantify the leaching rates of metal and selenium from the catalysts normalized by the catalyst masses ($\mu\text{mol g}_{catalyst}^{-1} \text{h}^{-1}$). The ratio between the Co and Se leaching rates of the less stable c-CoSe₂ is close to the 1:2 stoichiometry (FIG. 3c and Table 2). This suggests the leaching of c-CoSe₂ could be initiated by the surface oxidation of Se₂²⁻ to the soluble SeO_x due to the preferential affinity of O* to its Se site (FIG. 2c), followed by the near-stoichiometric dissolution of Co²⁺ from the surface. In contrast, the Se leaching from the more stable c-NiSe₂ is not only substantially suppressed compared to c-CoSe₂, but also slower than the Ni leaching (FIG. 3c). These suggest the leaching of c-NiSe₂ could mainly result from the preferential adsorption of both O* and OH* onto Ni (FIG. 2c) and the subsequent acid-base reaction with the electrolyte to dissolve Ni²⁺. This hypothesis is supported by the slower leaching of c-NiSe₂ under the less acidic pH of ~2.8 (FIG. 3c), and future studies will be helpful for confirming the catalyst leaching mechanisms. These in-depth catalyst leaching studies further confirm the enhanced stability of c-NiSe₂ for acidic 2e ORR.

TABLE 1

Comparisons of the normalized Ni and Se leaching rates from RRDE stability tests of c-NiSe ₂ (where H ₂ O ₂ accumulation is negligible) vs. H ₂ O ₂ bulk electroynthesis of c-NiSe ₂ /CFP (with steady accumulation of H ₂ O ₂), which are comparable and thus confirm that NiSe ₂ 's stability is maintained in the presence of dilute H ₂ O ₂ oxidant.				
Experiment	Catalyst	Electrolyte	Normalized Ni Leaching Rate ($\mu\text{mol}_{Ni} \text{g}_{catalyst}^{-1} \text{h}^{-1}$)	Normalized Se Leaching Rate ($\mu\text{mol}_{Se} \text{g}_{catalyst}^{-1} \text{h}^{-1}$)
RRDE Stability Test	c-NiSe ₂	O ₂ -saturated 0.05M H ₂ SO ₄ (pH ~1.2)	17.2 ± 5.6 ^[1]	5.77 ± 2.86 ^[1]
		O ₂ -saturated 0.1M NaHSO ₄ /Na ₂ SO ₄ (pH ~2.8)	6.64 ± 0.68 ^[1]	4.54 ± 0.78 ^[1]
H ₂ O ₂ Bulk Electro-synthesis	c-NiSe ₂ /CFP	O ₂ -saturated 0.05M H ₂ SO ₄ (pH~1.2)	9.9 ^[2]	9.0 ^[2]
		O ₂ -saturated 0.1M NaHSO ₄ /Na ₂ SO ₄ (pH ~2.8)	6.2 ^[2]	5.2 ^[2]

^[1] These avg. ± std. dev. leaching rates come from four RRDE stability tests of c-NiSe₂ at different catalyst loadings in each electrolyte, as tabulated in Table 2.

^[2] These leaching rates come from the initial H₂O₂ bulk electroynthesis run of c-NiSe₂/CFP at 0.60 V vs. RHE in each electrolyte, as shown in FIG. 23d.

TABLE 2

ICP-MS analyses of the spent electrolytes after the RRDE stability tests of c-NiSe ₂ and c-CoSe ₂ catalysts at various catalyst loadings in 0.05M H ₂ SO ₄ (PH ~1.2) and 0.1M NaHSO ₄ /Na ₂ SO ₄ (PH~2.8) solutions (see FIG. 3c).					
Electrolyte	Ex	Catalyst	Catalyst Loading ($\mu\text{g}_{\text{metal}} \text{cm}^{-2} \text{disk}$)	Electrolyte Volume (mL)	Time (h)
O ₂ -saturated 0.05M H ₂ SO ₄ (pH ~1.2)	1	c-NiSe ₂	229	41.0	4.0
	2		305	42.5	3.9
	3		381	41.0	4.0
	4		458	41.5	4.0
	5		—	—	—
	6	c-CoSe ₂	76	45.0	4.1
	7		114	42.0	4.0
	8		152	43.0	4.2
	9		229	44.5	4.1
	10		—	—	—
O ₂ -saturated 0.1M NaHSO ₄ / Na ₂ SO ₄ (pH ~2.8)	11	c-NiSe ₂	152	42.5	4.1
	12		229	41.5	4.0
	13		305	41.0	4.0
	14		381	43.0	4.0
	15		—	—	—
	16	c-CoSe ₂	76	41.5	4.0
	17		114	40.0	4.0
	18		152	41.5	4.0
	19		229	41.5	4.0
	20		—	—	—

Electrolyte	Ex	Catalyst	[Metal] (ppb)	[Se] (ppb)	Normalized Metal Leaching Rate ($\mu\text{mol}_{\text{metal}} \text{g}_{\text{catalyst}}^{-1} \text{h}^{-1}$)	Normalized Se Leaching Rate ($\mu\text{mol}_{\text{Se}} \text{g}_{\text{catalyst}}^{-1} \text{h}^{-1}$)
O ₂ -saturated 0.05M H ₂ SO ₄ (pH ~1.2)	1	c-NiSe ₂	7.75	2.75	12.8	3.38
	2		10.6	3.74	13.8	3.62
	3		17.2	9.02	17.0	6.63
	4		30.5	15.4	25.2	9.45
	5		—	—	Avg. \pm Std. Dev. = 17.2 \pm 5.6	Avg. \pm Std. Dev. = 5.77 \pm 2.86
	6	c-CoSe ₂	2.93	5.31	15.5	21.0
	7		5.69	11.0	19.0	27.6
	8		8.91	19.6	21.9	35.9
	9		13.6	27.8	23.5	35.9
	10		—	—	Avg. \pm Std. Dev. = 20.0 \pm 3.5	Avg. \pm Std. Dev. = 30.1 \pm 7.2
O ₂ -saturated 0.1M NaHSO ₄ / Na ₂ SO ₄ (pH ~2.8)	11	c-NiSe ₂	2.44	2.15	6.15	4.03
	12		3.62	3.06	6.06	3.82
	13		6.15	6.07	7.54	5.53
	14		6.55	6.22	6.79	4.79
	15		—	—	Avg. \pm Std. Dev. = 6.64 \pm 0.68	Avg. \pm Std. Dev. = 4.54 \pm 0.78
	16	c-CoSe ₂	3.37	6.32	17.0	23.9
	17		4.98	8.42	16.1	20.4
	18		9.62	19.2	24.1	36.0
	19		22.8	53.6	38.5	67.6
	20		—	—	Avg. \pm Std. Dev. = 23.9 \pm 10.3	Avg. \pm Std. Dev. = 37.0 \pm 21.5

Bulk Electrosynthesis of H₂O₂ in Acidic Solution Using c-NiSe₂ Cathode

[0139] We further performed constant-potential bulk electrosynthesis using integrated electrodes of c-NiSe₂ nanosheets directly grown on carbon fiber paper (NiSe₂/CFP, FIG. 16) to accumulate H₂O₂ in O₂-saturated 0.05 M H₂SO₄ in a two-compartment three-electrode H-cell (FIG. 17) at various applied potentials ranging from 0.50 to 0.65

V vs. RHE (FIG. 3d and FIG. 18). Both the cumulative H₂O₂ yield and selectivity after 6 hours of bulk electrosynthesis are potential-dependent, and peak at the optimum potential of 0.60 V vs. RHE (FIG. 3d). Cyclic voltammograms recorded before and after each electrosynthesis trial suggest additional cathodic current is generated on NiSe₂/CFP after the accumulation of H₂O₂ in the solution (FIG. 18), likely due to the electroreduction of H₂O₂ to water as the Faradaic side reaction.

[0140] To understand this potential-dependent electro-synthesis of H_2O_2 , we studied the side reaction of H_2O_2 electroreduction in competition with 2e^- ORR on c-NiSe₂ catalyst drop-casted on RRDE. In 0.05 M H_2SO_4 , the catalytic onset potential of H_2O_2 electroreduction on c-NiSe₂ coincides with that of 2e^- ORR, and the rate of H_2O_2 electroreduction increases with higher overpotential and H_2O_2 concentration (FIG. 19a). Therefore, as H_2O_2 concentration builds up, the net rate of H_2O_2 production (i.e., the production rate minus the electroreduction rate of H_2O_2) on c-NiSe₂ is positive only in a certain potential range and displays a parabolic trend peaking at an optimum potential (FIG. 19b). Similarly, H_2O_2 electroreduction also occurs on c-CoSe₂ but it affects the net production rate less because c-CoSe₂ exhibits a more positive catalytic onset potential for 2e^- ORR (FIG. 19 and FIG. 3a). A similar parabolic trend in the net rate of H_2O_2 production on c-NiSe₂ is observed in 0.1 M $\text{NaHSO}_4/\text{Na}_2\text{SO}_4$ buffer at pH~2.8 (FIG. 20). These results show the importance of considering H_2O_2 electroreduction and operating NiSe₂/CFP at the optimum applied potential for H_2O_2 electro-synthesis.

[0141] We demonstrated sustained bulk electro-synthesis of H_2O_2 in O_2 -saturated 0.05 M H_2SO_4 at the optimum 0.60 V vs. RHE using one NiSe₂/CFP electrode repeatedly for five consecutive runs over 37 hours (FIG. 3e). Since the cathodic current on NiSe₂/CFP gradually increased over time because of the electroreduction of the accumulated H_2O_2 , we replaced the catholyte with fresh H_2O_2 -free electrolyte between runs to maintain the steady net production of H_2O_2 (FIG. 21). Over the initial 2-hour period of each run, the NiSe₂/CFP electrode consistently accumulated 203 ± 10 ppm H_2O_2 and produced 15.4 ± 1.4 μmol H_2O_2 with a cumulative H_2O_2 selectivity of $51.8 \pm 1.8\%$ with no obvious decay (FIG. 3e and FIG. 21). A higher H_2O_2 yield of 34.8 ± 2.8 μmol and a higher accumulated concentration of 661 ± 53 ppm were achieved over a longer period of 7.4 ± 0.5 hours at the end of each run, but with a lower H_2O_2 selectivity of $30.8 \pm 1.2\%$ (FIG. 3e and FIG. 21). NiSe₂/CFP shows a similar H_2O_2 electro-synthesis performance in O_2 -saturated 0.1 M $\text{NaHSO}_4/\text{Na}_2\text{SO}_4$ buffer at pH~2.8 (FIG. 22). The spent NiSe₂/CFP electrode is structurally and compositionally stable after H_2O_2 electro-synthesis (FIG. 23), and catalyst leaching studies confirm that NiSe₂'s stability is maintained in the presence of dilute H_2O_2 oxidant (Table 1). These experiments suggest that the unavoidable electroreduction of H_2O_2 could limit the maximum accumulated concentration of H_2O_2 and the overall selectivity practically achievable using these new earth-abundant electrocatalysts, however, the electro-Fenton process of converting H_2O_2 to OH may allow us to utilize the produced H_2O_2 as an oxidant more efficiently by circumventing the undesired H_2O_2 electroreduction to water.

Glycerol Valorization Via the Electro-Fenton Process at c-NiSe₂ Cathode

[0142] To enable glycerol valorization by the electro-Fenton process, we operated NiSe₂/CFP cathode at the fixed

potential of 0.60 V vs. RHE in O_2 -saturated 0.1 M $\text{NaHSO}_4/\text{Na}_2\text{SO}_4$ buffer (pH~2.8) containing Fe^{2+} and glycerol. The balanced equation shows that cathodic glycerol conversion consumes protons (FIG. 4a). To maintain the proton balance and stabilize the acidic pH in the cathodic half-cell, it is critical to place 0.05 M H_2SO_4 in the anode compartment to transport protons through the Nafion membrane (FIG. 24). We used proton and carbon-13 nuclear magnetic resonance (^1H and ^{13}C NMR) to identify and quantify the many possible C_3 , C_2 , and C_1 products that can be sequentially formed from the oxidation of glycerol (FIG. 4b). Control experiments show that the electro-generated H_2O_2 itself is not capable of oxidizing glycerol without the presence of Fe^{2+} , which confirms that the electro-Fenton process is indeed responsible for glycerol valorization at the cathode.

[0143] We further studied the impact of Fe^{2+} concentration ($[\text{Fe}^{2+}]$) on the glycerol valorization via the electro-Fenton process. The rate of OH formation from the Fenton reaction should increase with higher $[\text{Fe}^{2+}]$ based on the rate law, but too much Fe^{2+} would consume the formed OH and decrease the oxidizing power ($\text{Fe}^{2+} \cdot \text{OH} + \text{H}^+ \rightarrow \text{Fe}^{3+} + \text{H}_2\text{O}$). After a controlled amount of charge is passed through NiSe₂/CFP cathode at 0.60 V vs. RHE, high glycerol conversion is achieved when $[\text{Fe}^{2+}]$ is 0.5 mM or 1.0 mM, while too little Fe^{2+} (0.1 mM) results in low glycerol conversion likely due to the slow OH formation (FIG. 4c). On the other hand, the selectivity toward all detected C_3 products [glyceraldehyde (GLAD), dihydroxyacetone (DHA), glyceric acid (GLA)] remain relatively high when $[\text{Fe}^{2+}]$ is 1.0 mM or below but decreases substantially when $[\text{Fe}^{2+}]$ is increased to 2.5 mM (FIG. 4c). One possible explanation is that at high $[\text{Fe}^{2+}]$, the high $\cdot\text{OH}$ formation rate increases the relative concentration of $\cdot\text{OH}$ to glycerol locally near the cathode, which might not be effectively dissipated even under vigorous stirring, driving the glycerol oxidation further to primarily C_2 [glycolaldehyde (GAD), glycolic acid (GA), glyoxylic acid (GLOA)] and C_1 [formic acid (FA)] products. This could also explain the relatively low glycerol conversion when $[\text{Fe}^{2+}]$ is 2.5 mM despite the fast OH formation rate (FIG. 4c). Overall, we identified 0.5 mM as the optimum $[\text{Fe}^{2+}]$ to concurrently achieve high glycerol conversion of up to ~55% and high C_3 product selectivity for cathodic valorization of glycerol (FIG. 4d and Table 3). As more charge is passed, the glycerol conversion steadily increases but the C_3 product selectivity decreases slightly due to the sequential oxidation of intermediate products. The gradual loss in the carbon balance of all detected aqueous phase organic products likely results from the eventual oxidation of FA to gaseous CO_2 undetectable by NMR (vide infra). The spent NiSe₂/CFP cathode was shown to be structurally and compositionally stable after the electro-Fenton process (FIG. 27). These observations suggest that achieving an efficient electro-Fenton production of OH but maintaining a moderate concentration of this strongly oxidizing radical is the key to achieving high C_3 product selectivity and conversion from glycerol

TABLE 3

Summary of the aqueous phase organic (C ₃ , C ₂ , and C ₁) product selectivity, glycerol conversion percentage, and carbon balance and Faradaic efficiency of all detected aqueous phase organic products for glycerol valorization in the cathodic half-cell via the electro-Fenton process at c-NiSe ₂ /CFP cathode and the direct anodic oxidation at Pt/C anode.										
Half-Cell Studies	Example	Starting Volume (mL)	Starting [Glycerol] (mM)	Starting [Fe ²⁺] (mM)	Starting pH	Charge Passed (C)	Final Volume (mL)	Final [Glycerol] (mM)	Final pH	Glycerol Conversion (%)
Electro-Fenton Process at c-NiSe ₂ Cathode	1	4	50.6	0.1	2.79	14.6	3.23	58.5	2.11	6.6
	2	4	50.6	0.1	2.79	29.3	2.66	63.3	2.06	16.9
	3	4	50.6	0.1	2.79	43.9	2.39	61.5	1.96	27.4
	4	4	50.5	0.5	2.85	14.6	3.27	52.2	2.19	15.6
	5	4	50.5	0.5	2.83	29.2	2.38	51.1	2.01	39.8
	6	4	50.5	0.5	2.85	43.9	2.05	44.4	1.95	54.9
	7	4	50.6	1.0	2.80	14.6	3.42	45.0	2.20	22.3
	8	4	50.6	1.0	2.80	29.3	2.87	41.6	2.08	39.8
	9	4	50.6	1.0	2.81	43.9	2.61	34.2	2.03	55.0
	10	4	50.5	2.5	2.84	14.6	3.14	53.7	2.16	13.8
	11	4	50.5	2.5	2.86	29.2	2.62	54.8	2.08	26.6
	12	4	50.5	2.5	2.85	43.9	2.08	59.5	1.94	36.8
Direct Anodic Oxidation at Pt/C Anode	13	4	51.1	—	1.21	14.8	3.49	45.6	1.15	22.2
	14	4	51.1	—	1.21	29.7	3.00	39.7	1.09	41.8
Pt/C Anode	15	4	51.9	—	1.21	45.1	2.20	36.9	0.95	60.9

Half-Cell Studies	Example	Aqueous Phase Organic Product Selectivity (%) ^[1]								Carbon	
		C ₃				C ₂			C ₁	Balance (%)	Efficiency (%) ^[2]
		GLAD	DHA	GLA	HPA	GAD	GA	GLOA	FA		
Electro-Fenton Process at c-NiSe ₂ Cathode	1	37.7	17.1	1.3	—	7.4	2.7	0.7	5.4	98.2	16.8
	2	33.3	13.9	1.9	—	4.7	3.0	0.4	7.5	94.1	21.3
	3	27.0	12.3	2.3	—	4.6	3.7	0.3	9.3	88.9	23.4
	4	50.2	20.6	2.3	—	9.1	3.0	1.0	10.7	99.5	57.6
	5	34.5	13.8	2.0	—	6.6	2.6	1.6	8.0	87.7	55.3
	6	29.6	12.4	3.2	—	6.6	3.5	1.3	9.5	81.3	52.1
	7	38.3	15.1	1.3	—	7.5	2.6	0.4	10.4	94.6	67.6
	8	31.1	13.9	2.2	—	7.2	2.9	0.5	11.9	88.0	60.3
	9	28.1	12.7	2.9	—	7.0	3.2	1.5	12.4	82.3	57.3
	10	11.2	7.5	1.2	—	7.8	7.3	0.4	37.8	96.3	73.5
	11	9.0	6.3	1.1	—	6.4	7.6	0.3	36.7	91.3	67.6
	12	7.9	5.6	1.5	—	6.0	8.5	0.4	37.6	88.0	64.0
Direct Anodic Oxidation at Pt/C Anode	13	37.2	7.0	43.6	0.7	—	3.9	—	0.2	98.4	85.1
	14	29.1	5.1	37.6	0.6	—	4.5	—	0.3	90.4	68.6
Pt/C Anode	15	20.4	4.5	39.9	0.9	—	3.2	—	0.1	80.6	62.6

^[1] GLAD = glyceraldehyde; DHA = dihydroxyacetone; GLA = glyceric acid; HPA = hydroxypyruvic acid; GAD = glycolaldehyde; GA = glycolic acid;

GLOA = glyoxylic acid; FA = formic acid;

^[2] See Examples for details in the Faradaic efficiency calculation.

Pairing the Electro-Fenton Process with Anodic Oxidation for Glycerol Valorization.

[0144] To valorize glycerol at both cathode and anode concurrently, anodic glycerol oxidation needs to operate in acidic solution to match the pH requirement of the electro-Fenton process. Therefore, anodic glycerol oxidation was performed in an Ar-saturated H₂SO₄ solution containing 50 mM glycerol on an anode made by drop-casting commercial Pt/C catalyst on carbon fiber paper. This paired system needs to operate in a two-compartment H-cell rather than in an undivided cell because the O₂ needed for the electro-Fenton process can undergo undesirable ORR on the Pt/C anode. Protons are transported through Nafion membrane and stabilize the pH of the catholyte (O₂-saturated NaHSO₄/Na₂SO₄ buffer containing 50 mM glycerol and 0.5 mM Fe²⁺, pH~2.8) where the electro-Fenton process takes place.

[0145] Anodic glycerol oxidation at Pt/C anode in 0.05 M H₂SO₄ was first evaluated in the half-cell (FIG. 28). To mimic the operation of the paired system, we applied a constant current of 1.7 mA (FIG. 28c) to approximately match with the current on NiSe₂/CFP cathode in the electro-Fenton half-cell studies. After a controlled amount of charge

was passed, the applied potential of Pt/C anode was relatively stable around 0.55 V vs. RHE, and glycerol was selectively oxidized into C₃ products [GLAD, DHA, GLA, hydroxypyruvic acid (HPA)] with very small quantities of C₂ (GA) and C₁ (FA) products (FIG. 28e and Table 3). The anodic half-cell studies show the viability of valorizing glycerol in a linear paired electrochemical system that theoretically could operate at a negligible external bias (<0.05 V) with little external energy input needed if the internal resistance is negligible (discussion provided in the Detailed Description).

[0146] We then demonstrated the proof-of-concept linear paired electrochemical valorization of glycerol by feeding glycerol in both cathode and anode compartments of the H-cell where NiSe₂/CFP cathode was operated at 0.60 V vs. RHE and Pt/C anode matched the current (FIGS. 29 and 30). With 0.1 M NaHSO₄/Na₂SO₄ catholyte and 0.05 M H₂SO₄ anolyte, the paired system operated steadily at an external bias around 1 V (FIG. 5a, Condition 1), and the product distributions in the catholyte and anolyte (FIG. 5b, Condition 1) closely resembled those found in the respective half-cell studies under similar conditions, i.e., high percent-

age of C_3 products. This external bias is higher than the theoretical value because there is a large solution IR drop between the anode and the reference electrode located on opposite sides of the membrane (FIG. 30a).

[0147] When a higher supporting electrolyte concentration of 0.5 M was applied for both catholyte and anolyte, the paired system operated at a much lower external bias below 0.2 V (FIG. 5a, Condition II) due to the greatly reduced solution IR drop at the anode (FIG. 30b). After a controlled amount of charge was passed, the product distributions in the anolyte were mostly unaffected (FIG. 5b, Condition II), whereas the detected aqueous phase organic products in the catholyte slightly decreased. The C_3 product selectivity in both catholyte and anolyte of the paired system decreased with increasing glycerol conversion up to ~53% (FIG. 5b and Table 5), due to the sequential oxidation of intermediate products, similar to the respective half-cell studies (vide supra). Since FA was detected as a late-stage oxidation product in both catholyte and anolyte (Table 5), control experiments suggested that both the electro-Fenton process and the anodic oxidation could further oxidize FA into gaseous CO_2 , which may account for the loss in the carbon balance of all detected aqueous products in both catholyte and anolyte. Finally, we note that the residual excess external bias of 0.2 V for this paired system appears to be mostly caused by the internal resistance, and the overall paired process can be viewed as a controlled partial oxidation of glycerol by oxygen gas, which should be thermodynamically spontaneous. By employing zero-gap cell designs involving membrane electrode assemblies to lower the ohmic overpotential and by designing more active cathode and anode electrocatalysts to lower the kinetic overpotentials further, we believe that paired electrochemical systems for efficient glycerol valorization that need no external bias and no external energy input could be realized.

Summary

[0148] In summary, we demonstrated a linear paired electrochemical process for concurrent glycerol valorization by the electro-Fenton process at a stable and earth-abundant cathode together with direct oxidation at an anode. This process is enabled by the development of highly selective and stable $2e^-$ ORR catalyst for H_2O_2 production in acidic solution, which is elucidated by calculated free energy diagrams and surface adsorbate analyses and experimentally shown with RRDE and catalyst leaching studies together with sustained electrosynthesis of H_2O_2 . The electro-Fenton process at the cathode at the demonstrated operation conditions leads to efficient cathodic glycerol valorization with a high selectivity toward valuable C_3 oxidation products and high glycerol conversion of 55%. The linear paired system achieves similarly high glycerol conversion and product selectivity and can operate at a very small external bias below 0.2 V, which could be made into an unbiased system after further optimization in the future. The design principles for stable and selective electrocatalysts for acidic H_2O_2 production and the electro-Fenton process, and the conceptual strategy of linear pairing the electro-Fenton process with anodic oxidation presented here open up new opportunities for electrochemical valorization of a variety of biomass feedstocks with high atom efficiency and low energy cost.

Methods and Materials

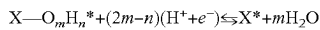
Computational Method

[0149] Spin polarized electronic structure calculations were performed using the Vienna Ab initio Simulation package (VASP) interfaced with the Atomic Simulation Environment (ASE). Projector augmented wave (PAW) pseudopotentials with a cutoff of 450 eV were used to treat core electrons, and the Perdew-Burke-Ernzerhof (PBE) functional was used to treat exchange and correlation. Dispersion was treated using Grimme's D3(ABC) method. To better describe the Co 3d electrons in c-CoSe₂, a Hubbard U parameter, $U_{eff}=2.0$ eV, was taken from a previous report. A variety of Hubbard U parameters were tested for c-NiSe₂, and were found to have little to no effect on the geometries or energies; therefore, no Hubbard U parameter was used for this catalyst. Solvation effects were treated using the continuum solvent method VASPsol. The Brillouin zone was sampled using a (10, 10, 10) and (10, 10, 1) Γ -centered Monkhorst-Pack mesh for bulk and surface calculations, respectively. Lattice constants were determined by fitting to an equation of state (EOS).

[0150] For both c-NiSe₂ and c-CoSe₂, their respective (100) surface exhibits the lowest surface energy compared to other crystal surfaces, and thus is the most thermodynamically stable surface [0.044 vs. 0.064 vs. 0.069 eV \AA^{-2} for c-CoSe₂ (100) vs. (110) vs. (111) surface; 0.036 vs. 0.053 vs. 0.058 eV \AA^{-2} for c-NiSe₂ (100) vs. (110) vs. (111) surface]. The (100) surfaces of c-NiSe₂ and c-CoSe₂ were modelled as a 1x1 unit cell slab with two repeats in the z-direction, leading to a total of 8 metal atoms and 16 Se atoms and a vacuum gap of at least 15 \AA . The top half of the slabs was allowed to relax while the bottom half was frozen to simulate the bulk. For each ionic configuration, the electronic energy was converged below 10^{-6} eV. Both the clean slab and adsorbates were allowed to relax until the forces were converged below 0.005 eV \AA^{-2} . Transition states were located using the nudged elastic band (NEB) method and were refined using the dimer method. All transition states were confirmed saddle points with one imaginary frequency corresponding to bond breaking.

[0151] Binding energies were calculated with respect to O_2 (g) and H^+ (aq) and e^- . The energy of H^+ (aq) and e^- was calculated using the computational hydrogen electrode (CHE) method, where H^+ (aq) is assumed to be in thermodynamic equilibrium with H_2 (g). The use of the CHE method for our calculation is validated by the fact that the difference in the OOH* binding energy on the c-NiSe₂ (100) surface calculated by the CHE method vs. the grand-canonical density functional theory (GC-DFT) method, accounting for the change in surface charge density upon adsorption, is <0.1 eV and can be safely neglected. In order to avoid well-known errors in the DFT treatment of O_2 (g), the free energy of O_2 (g) was determined by matching the experimental standard equilibrium potential (1.229 V) of the reaction $\frac{1}{2} O_2$ (g) + $2 H^+$ (aq) + $2 e^- \rightarrow H_2O$ (l). The adsorption of O_2 , forming O_2^* from O_2 (g), is excluded from our calculation because DFT does not treat O_2 (g) accurately, and the estimated free energy difference between O_2 (g) and O_2^* on the c-NiSe₂ (100) surface is <0.1 eV and can be safely neglected. The free energies of species were calculated using $G=H-T\cdot S$, where H is the enthalpy including zero-point energy (ZPE) and thermal corrections, and S is either the total experimental entropy at 298 K and 1 bar (for gas phase

species) or calculated under the harmonic approximation taking into account both vibrational contributions and hindered translations/rotations (for surface bound species). The free energy of $\text{H}_2\text{O}_{(l)}$ was calculated using the experimental free energy of formation for $\text{H}_2\text{O}_{(l)}$ and $\text{H}_2\text{O}_{(g)}$. The solvation free energy of $\text{H}_2\text{O}_2_{(aq)}$ was calculated using the experimental Henry's law constant. The calculated standard equilibrium potential (U_{RHE}^o) of the $2e^-$ ORR reaction $\text{O}_2_{(g)} + 2\text{H}^+_{(aq)} + 2e^- \rightarrow \text{H}_2\text{O}_2_{(aq)}$ is 0.81 V, slightly higher than the experimental standard equilibrium potential of 0.69 V. **[0152]** Free energies of different surface adsorbate coverages were calculated to predict the most thermodynamically stable surface termination of each catalyst for a given set of potential and pH conditions under the assumption that the surfaces can be approximated in equilibrium with $\text{H}_2\text{O}_{(l)}$. The equilibrated proton-coupled electron transfer reaction for a general surface intermediate can then be written as:



where X is the surface binding site, m is the number of oxygen atoms, and n is the number of hydrogen atoms. The free energy of this reaction can be written as:

$$\Delta G(U, pH) = G_{\text{X}^*} + mG_{\text{H}_2\text{O}} - G_{\text{X}-\text{O}_m\text{H}_n^*} - (2m-n)(G_e + G_{\text{H}^+})$$

[0153] Using the computational hydrogen electrode (CHE) method ($G_e + G_{\text{H}^+} = \frac{1}{2}G_{\text{H}_2} - U_{SHE} - 2.303 k_B \cdot T \cdot \text{pH}$) and converting the standard hydrogen electrode (SHE) to the reversible hydrogen electrode (RHE) ($U_{RHE} = U_{SHE} + 2.303 k_B \cdot T \cdot \text{pH}$), the free energy can be rewritten as a function of U_{RHE} :

$$\Delta G(U_{RHE}) = G_{\text{X}^*} + mG_{\text{H}_2\text{O}} - G_{\text{X}-\text{O}_m\text{H}_n^*} - (2m-n)(\frac{1}{2}G_e - U_{RHE})$$

[0154] A 1×1 unit cell slab of the (100) surface of each catalyst that has two metal binding sites and four Se binding sites was used to model intermediate surface coverages as a function of potential. For c-NiSe₂, the Ni site is the preferential binding site for both OH* and O*. For c-CoSe₂, the Co site is the preferential binding site for OH*, and the Se site is the preferential binding site for O*. A wide variety of surface coverages were examined on various combinations of binding sites. For the sake of clarity, only the most thermodynamically stable surface coverages (in the U_{RHE} range of 0 V to 0.95 V) on the most preferential combination of binding sites were shown in FIG. 2c.

Chemicals

[0155] All chemicals were purchased from Sigma-Aldrich and used as received without further purification, unless noted otherwise. Deionized nanopure water (18.2 MΩ·cm) from Thermo Scientific Barnstead water purification systems was used for all experiments.

Materials Synthesis

[0156] c-NiSe₂ powder sample was prepared by a hydrothermal method. Following a procedure modified from a previous report, nickel hydroxide [Ni(OH)₂] precursor was first synthesized by dissolving 451.3 mg of NiSO₄·6H₂O (Acros Organics, 98+%) in 58.3 mL of water and 8.75 mL of 2 M ammonia aqueous solution (diluted from ammonium hydroxide solution, 28.0-30.0% NH₃ basis), and heating the solution at 180° C. for 24 h in a sealed 100-mL Teflon-lined stainless-steel autoclave. The resulting Ni(OH)₂ precursor

was hydrothermally converted into c-NiSe₂ as follows: 4.29 g of NaOH (≥97.0%) and 571 mg of Se powder (≥99.5%) were suspended in 50 mL of water via sonication and heated at 220° C. for 24 h in a sealed 80-mL autoclave; upon cooling to room temperature, 35 mg of Ni(OH)₂ precursor was suspended in 10 mL of water and added dropwise into the Se-containing solution under vigorous stirring, and then heated at 180° C. for additional 24 h in the same autoclave. The as-converted c-NiSe₂ product was successively washed with water, 1.25 M aqueous solution of Na₂S (nonahydrate, ≥98.0%) (to dissolve the elemental Se impurity), and water four times for each washing step, and dried under vacuum at 50° C.

[0157] To prepare Ni(OH)₂ precursor on carbon fiber paper (Ni(OH)₂/CFP), Teflon-coated carbon fiber paper (Fuel Cell Earth, TGP-H-060) was first treated with oxygen plasma at 150 W power for 5 min for each side and annealed in air at 700° C. for 5 min. A 3 cm×6 cm piece of annealed CFP was placed in the solution made of 2.1 mmol of Ni(NO₃)₂·6H₂O (≥97.0%), 4.2 mmol of NH₄F (≥98.0%), and 10.5 mmol of urea (99.0-100.5%) in 80 mL of water, and heated at 110° C. for 5 h in a sealed 100-mL autoclave. NiSe₂/CFP was prepared by the same hydrothermal selenization method described above, except for using a 1.5 cm×6 cm piece of Ni(OH)₂/CFP as the precursor. The as-converted NiSe₂/CFP was immersed in 1.25 M aqueous solution of Na₂S three times to remove any excess elemental Se, rinsed with water and ethanol, and dried under N₂ gas flow. The areal loading of c-NiSe₂ grown on CFP was determined by the mass change of CFP after the materials growth. The c-CoSe₂ samples were prepared following the published procedures. All catalyst samples were stored in an argon-filled glove box to minimize the exposure to air.

Materials Characterization

[0158] Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 ADVANCE powder X-ray diffractometer using Cu Kα radiation. Scanning electron microscopy (SEM) was performed on a Zeiss SUPRA 55VP field emission scanning electron microscope at an accelerating voltage of 1 kV. For SEM imaging, powder samples were drop-casted onto silicon wafer substrates. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific K-Alpha XPS system with an Al Kα X-ray source. Raman spectroscopy was performed on a Thermo Fisher Scientific DXR3xi Raman Imaging Microscope using a 50 m confocal pinhole aperture and a 532 nm laser source and with a low laser power of 0.1 mW and an exposure time of 1.0 second to avoid sample degradation. For XPS and Raman experiments, powder samples were drop-casted onto graphite substrates, which were made by cutting thin slices of graphite rod (Graphite Store, low wear EDM rod), abrading with 600 grit silicon carbide paper (Allied High Tech Products), and sonicating in water and ethanol until clean. X-ray absorption spectroscopy (XAS) of NiSe₂/CFP before and after electrochemical testing was performed in transmission mode at the Advanced Photon Source (APS) Beamline 10-BM-B, and analyzed using ATHENA and ARTEMIS software.

Electrode Preparation

[0159] Drop-casted catalysts were prepared on a rotating ring-disk electrode (RRDE-3A, ALS Co., Ltd) made of a glassy carbon disk (with a geometric area of $0.126 \text{ cm}^2_{\text{disk}}$) surrounded by a Pt ring. The collection efficiency of the bare RRDE was 0.43, determined experimentally using the ferri-/ferrocyanide redox couple. The RRDE was successively polished with 1, 0.3, and 0.05 m alumina suspensions (Allied High Tech Products) on a polishing cloth (Buehler, MicroCloth), thoroughly rinsed with water and methanol, briefly sonicated in methanol for <20 s, and dried under ambient conditions before use. The catalyst inks were prepared by suspending pre-weighed catalyst powders in desired volumes of a 9:1 (v/v) mixture of water and 5 wt % Nafion solution by sonication for 1 h. A fixed volume (10 μL) of catalyst ink was then drop-casted on the disk electrode and dried under ambient conditions at a rotation rate of 700 rpm to form a uniform catalyst film where the Nafion loading was identical ($0.4 \text{ mg}_{\text{Nafion}} \text{ cm}^{-2}_{\text{disk}}$) whereas the catalyst loading was varied (FIGS. 3a and 3b). NiSe₂/CFP cathode was fabricated from as-synthesized NiSe₂/CFP sample (vide supra) by using 5-min epoxy (Devcon) to define the exposed geometric area as $\sim 1 \text{ cm} \times \sim 1 \text{ cm}$. The Pt/C anode was prepared by on drop-casting 200 μL of the catalyst ink (50 mg of 20 wt % Pt/C suspended in 900 μL of isopropanol and 100 μL of 5 wt % Nafion solution by sonication for 1.5 h) on both sides (100 μL on each side) of the pre-fabricated bare CFP electrode ($\sim 1 \text{ cm} \times \sim 1 \text{ cm}$), resulting in a catalyst loading of $\sim 2 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}_{\text{geo}}$.

Rotating Ring-Disk Electrode Measurement

[0160] RRDE measurements were conducted in an undivided three-electrode cell with a graphite rod counter electrode and a Hg/Hg₂SO₄ (saturated K₂SO₄) reference electrode (calibrated against a saturated calomel electrode) connected to a Bio-Logic VMP-300 multichannel potentiostat. All potentials were reported versus RHE (E vs. RHE=E vs. SHE+0.059×pH). Prior to RRDE measurements, the electrolyte solution (40-45 mL) of either 0.05 M H₂SO₄ (pH~1.2) or 0.1 M NaHSO₄/Na₂SO₄ buffer solution (pH~2.8) was purged with O₂ gas for >10 min, and a blanket of O₂ gas was maintained above the electrolyte solution during the measurements. Under O₂-saturated condition, the catalyst-coated disk was first conditioned by running cyclic voltammetry (CV) between -0.025 V and 0.75 V vs. RHE at 100 mV s⁻¹ and 1600 rpm for 10 cycles, while holding the Pt ring at 1.3 V vs. RHE. The Pt ring was then conditioned by running CV between 0.05 V and 1.20 V vs. RHE at 100 mV s⁻¹ and 1600 rpm for 10 cycles while holding the disk at 0.75 V vs. RHE to remove the surface PtO_x. The 2e⁻ ORR catalytic properties were evaluated by performing linear sweep voltammetry of the catalyst-coated disk from 0.75 to -0.025 V vs. RHE at 50 mV s⁻¹ and various rotation rates, meanwhile holding the Pt ring at 1.3 V vs. RHE. Finally, the background current, double-layer capacitance (C_{dl}, determined by CV of the disk between -0.025 V and 0.75 V vs. RHE at various scan rates and 0 rpm), and uncompensated resistance (Ru, determined by electrochemical impedance spectroscopy of the disk at 0.75 V vs. RHE) were measured

under Ar-saturated conditions. By manually conducting background current and iR corrections, the H₂O₂ selectivity (P_{RRDE}) is calculated as follows:

$$P_{RRDE}(\%) = \frac{2 \times \frac{i_{ring}}{N}}{i_{disk} + \frac{i_{ring}}{N}} \times 100\%$$

where i_{disk} and i_{ring} are the respective disk and ring current, and N is the collection efficiency. For the ease of visualizing the H₂O₂ selectivity from RRDE voltammograms (FIG. 3a), both disk and ring current densities (j_{disk} and j_{ring}) are normalized to the geometric area of the disk electrode (A_{disk}), and the ring current density is further adjusted by the collection efficiency:

$$j_{disk} = \frac{i_{disk}}{A_{disk}}$$

$$j_{ring} = \frac{i_{ring}}{A_{disk} \times N} = j_{peroxide}$$

where $j_{peroxide}$ is the partial current density for H₂O₂ production.

[0161] The protocols for long-term RRDE stability tests were described in FIG. 12. After these stability tests, the spent catalysts were recovered from the disk electrode by sonicating in water and ultracentrifuging at 13200 rpm for 1 min, followed by re-dispersing in minimal amount of water and drop-casting onto graphite substrates for XPS and Raman characterization (vide supra). To monitor the catalyst leaching during these stability tests, the spent electrolyte solutions were filtered with 0.22- μm syringe filters (Restek) and then analyzed with inductively coupled plasma mass spectrometry (ICP-MS) measurements on an Agilent 8900 Triple Quadrupole ICP-MS spectrometer. ICP-MS standard solutions were prepared by dissolving NiSO₄·6H₂O ($\geq 98\%$), or CoSO₄·7H₂O ($\geq 99\%$), or SeO₂ ($\geq 99.9\%$) in a matrix solution of 0.05 M H₂SO₄ (pH~1.2) or 0.1 M NaHSO₄/Na₂SO₄ (pH~2.8).

Bulk Electrosynthesis of H₂O₂

[0162] NiSe₂/CFP cathode (vide supra) was used for constant-potential bulk electrosynthesis of H₂O₂ in O₂-saturated 0.05 M H₂SO₄ (pH~1.2) or 0.1 M NaHSO₄/Na₂SO₄ (pH~2.8) solution (4 mL, stirred at 1200 rpm) placed in the cathode compartment of a two-compartment three-electrode H-cell (see FIG. 17). Nafion 117 membrane (Fuel Cell Store) was cleaned by successively immersing in 3 wt % H₂O₂, water, 1 M H₂SO₄, and water at 80° C. for 1 h for each cleaning step and stored in 0.05 M H₂SO₄ at room temperature before use. NiSe₂/CFP cathode was conditioned by running CV between -0.025 V and 0.75 V vs. RHE at 100 mV s⁻¹ for 5 cycles to reach the steady state before use. Chronoamperometry was then performed to produce H₂O₂ at NiSe₂/CFP cathode, and the optimum operating potential was found to

be 0.60 V vs. RHE (see FIG. 3d). A small aliquot (25 μ L) of catholyte was periodically sampled during chronoamperometry and mixed with 8 mL of $\text{Ce}(\text{SO}_4)_2$ stock solution (~ 0.4 mM Ce^{4+} in 0.5 M H_2SO_4 matrix solution) to chemically detect the produced H_2O_2 by UV-Vis spectrophotometry at 318 nm ($2 \text{Ce}^{4+} + \text{H}_2\text{O}_2 \rightarrow 2 \text{Ce}^{3+} + \text{O}_2 + 2 \text{H}^+$). The concentration of the produced H_2O_2 can be calculated as follows:

$$[\text{H}_2\text{O}_2] = \frac{8 \text{ mL} \times [\text{Ce}^{4+}]_{\text{before}} - 8.025 \text{ mL} \times [\text{Ce}^{4+}]_{\text{after}}}{2 \times 0.025 \text{ mL}}$$

where $[\text{H}_2\text{O}_2]$ is the cumulative H_2O_2 concentration, $[\text{Ce}^{4+}]_{\text{before}}$ and $[\text{Ce}^{4+}]_{\text{after}}$ are the $[\text{Ce}^{4+}]$ in the stock solution (determined by fitting to the standard curve) before and after mixing with the catholyte aliquot. The cumulative H_2O_2 yield ($n_{\text{H}_2\text{O}_2}$), H_2O_2 selectivity ($P_{\text{H}_2\text{O}_2}$), and Faradaic efficiency ($FE_{\text{H}_2\text{O}_2}$) are calculated based on $[\text{H}_2\text{O}_2]$, the catholyte volume (taking into account the evaporation), and the total amount of charge passed (Q_{total}) (see detailed methodology for these calculations described in our previous report):

$$P_{\text{H}_2\text{O}_2} (\%) = \frac{n_{\text{H}_2\text{O}_2} (\text{mol})}{n_{\text{H}_2\text{O}_2} (\text{mol}) + \frac{Q_{\text{total}} (\text{C}) - 2 \times n_{\text{H}_2\text{O}_2} (\text{mol}) \times F}{4 \times F}} \times 100\%$$

$$FE_{\text{H}_2\text{O}_2} (\%) = \frac{2 \times n_{\text{H}_2\text{O}_2} (\text{mol}) \times F}{Q_{\text{total}} (\text{C})} \times 100\%$$

where F is the Faraday constant (96485 C mol^{-1}). To monitor the catalyst leaching during H_2O_2 bulk electrosynthesis, the spent catholytes were filtered with 0.22- μm syringe filters (Restek) and diluted by 15 times with a matrix solution of 0.05 M H_2SO_4 for ICP-MS analysis (vide supra).

Glycerol Valorization and Product Analysis

[0163] All experiments of glycerol valorization were performed in the two-compartment three-electrode H-cell described above. Half-cell studies of glycerol valorization via the electro-Fenton process at NiSe_2 cathode were performed by chronoamperometry with controlled amounts of charge passed at 0.60 V vs. RHE in O_2 -saturated 0.1 M $\text{NaHSO}_4/\text{Na}_2\text{SO}_4$ solution (pH \sim 2.8) containing glycerol (~ 50 mM) and Fe^{2+} (0.1, 0.5, 1.0, or 2.5 mM, prepared from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\geq 99.0\%$) (see schematic in FIG. 24). Half-cell studies of direct oxidation of glycerol at Pt/C anode were performed by chronopotentiometry with controlled amounts of charge passed at 1.7 mA in Ar-saturated 0.05 M H_2SO_4 solution (pH \sim 1.2) containing glycerol (~ 50 mM) (see schematic in FIG. 28). Linear paired glycerol valorization at the NiSe_2 cathode (in O_2 -saturated 0.1 M or 0.5 M $\text{NaHSO}_4/\text{Na}_2\text{SO}_4$ solution containing ~ 50 mM glycerol and 0.5 mM Fe^{2+} , pH \sim 2.8) and Pt/C anode (in Ar-saturated H_2SO_4 solution containing ~ 50 mM glycerol) was performed by operating the cathode via chronoamperometry at 0.60 V vs.

RHE while recording the applied potential of the anode (see schematic in FIG. 29). The analysis of the products from glycerol valorization was performed by ^1H and ^{13}C NMR spectroscopy on a Bruker AVANCE III 600 MHz NMR spectrometer. Glycerol ($\geq 99.0\%$), DL-glyceraldehyde ($\geq 90\%$), dihydroxyacetone (Pharmaceutical Secondary Standard; Certified Reference Material), DL-glyceric acid (TCI America, 20% in water, ca. 2 mol/L), β -hydroxyppyruvic acid ($\geq 95.0\%$), tartronic acid (Alfa Aesar, 98%), sodium mesoxalate monohydrate ($\geq 98.0\%$), glycolaldehyde dimer (crystalline, mixture of stereoisomers), glycolic acid (99%), glyoxylic acid monohydrate (98%), oxalic acid (99.999%), and formic acid ($\geq 98\%$) were individually prepared into NMR standard samples (500 μ L) in Norell $\text{\textcircled{R}}$ Sample Vault Series TM NMR tubes (diam. \times L 5 mm \times 178 mm) using D_2O (99.9 atom % D) as the solvent and maleic acid (Standard for quantitative NMR, TraceCERT $\text{\textcircled{R}}$) as the internal standard. To achieve quantitative ^1H NMR results, the relaxation delay was set to 20 seconds (longer than 5 times of the T1 relaxation times of all compounds of interest determined by inversion recovery experiments). UW pulse sequence was used for the solvent suppression, and 4 scans were collected. For ^{13}C NMR results, the relaxation delay was set to 2 seconds, and 256 scans were collected. After the half-cell or linear paired glycerol valorization experiments, the catholytes and/or anolytes of interest were filtered with 0.22- μm syringe filters (Restek) and prepared into NMR samples accordingly. The quantifications of $[\text{glycerol}]_i$, $[\text{glycerol}]_f$, and $[\text{C}_n \text{ product}]_f$ are based on the selected ^1H NMR peak integration ratios relative to the maleic acid internal standard. The glycerol conversion, C_n product selectivity ($n=1, 2, 3$), and carbon balance of all detected aqueous phase organic products are calculated as follows:

$$\text{glycerol conversion } (\%) = \frac{[\text{glycerol}]_i \times V_i - [\text{glycerol}]_f \times V_f}{[\text{glycerol}]_i \times V_i} \times 100\%$$

C_n product selectivity (%) =

$$\frac{n}{3} \times \frac{[\text{C}_n \text{ product}]_f \times V_f}{[\text{glycerol}]_i \times V_i - [\text{glycerol}]_f \times V_f} \times 100\%$$

carbon balance (%) =

$$\frac{3 \times [\text{glycerol}]_f \times V_f + \sum_{n=1}^3 \{n \times [\text{C}_n \text{ product}]_f \times V_f\}}{3 \times [\text{glycerol}]_i \times V_i} \times 100\%$$

where V_i and V_f are the initial and final electrolyte volume, $[\text{glycerol}]_i$ and $[\text{glycerol}]_f$ are the initial and final concentration of glycerol, $[\text{C}_n \text{ product}]_f$ is the final concentration of C_n product ($n=1, 2, 3$), all of which are listed in Table 3 and 5. The Faradaic efficiency of all detected aqueous phase organic products at the anode (FE_{anode}) and the cathode (FE_{cathode}) are calculated and estimated, respectively, based on the methods described in below and these calculated FE_{anode} and estimated FE_{cathode} values are also listed in Table 3 and 5.

TABLE 4

Comparisons between the 183 μm -thick Nafion 117 membrane and the 89 μm -thick Nafion NE1035 membrane.					
Membrane	Thickness	Catholyte	Anolyte	R at Cathode	R at Anode
Nafion 117	183 μm	0.1M NaHSO ₄ /Na ₂ SO ₄ (pH ~2.8) + ~50 mM Glycerol + 0.5 mM Fe ²⁺	0.05M H ₂ SO ₄ + ~50 mM Glycerol	1.4 Ω (Run 1) ^[1]	713 Ω (Run 1) ^[1]
				1.3 Ω (Run 2) ^[1]	726 Ω (Run 1) ^[1]
				1.3 Ω (Run 3) ^[1]	722 Ω (Run 1) ^[1]
		0.5M NaHSO ₄ /Na ₂ SO ₄ (pH ~2.8) + ~50 mM Glycerol + 0.5 mM Fe ²⁺	0.5M H ₂ SO ₄ + ~50 mM Glycerol	0.8 Ω (Run 4) ^[2]	159 Ω (Run 4) ^[2]
				0.8 Ω (Run 5) ^[2]	166 Ω (Run 5) ^[2]
Nafion NE1035	89 μm	0.1M NaHSO ₄ /Na ₂ SO ₄ (pH ~2.8)	0.05M H ₂ SO ₄	2.2 Ω	685 Ω
		0.5M NaHSO ₄ /Na ₂ SO ₄ (pH ~2.8)	0.5M H ₂ SO ₄	1.8 Ω	173 Ω

^[1] See FIG. 30a.^[2] See FIG. 30b.

TABLE 5

Summary of the aqueous phase organic (C ₃ , C ₂ , and C ₁) product selectivity, glycerol conversion percentage, and carbon balance and Faradaic efficiency of all detected aqueous phase organic products for linear paired electrochemical valorization of glycerol at c-NiSe ₂ /CFP cathode and Pt/C anode.										
Supporting Electrolyte Condition (I or II)		Starting Volume (mL)	Starting [Glycerol] (mM)	Starting [Fe ²⁺] (mM)	Starting pH	Charge Passed (C)	Final Volume (mL)	Final [Glycerol] (mM)	Final pH	
										I
		Anolyte	4	53.1	—	1.21	15.0	3.58	48.1	1.29
	Run 2	Catholyte	4	50.4	0.5	2.89	30.0	2.80	44.7	1.85
		Anolyte	4	53.1	—	1.21	30.0	3.33	39.6	1.29
	Run 3	Catholyte	4	50.4	0.5	2.89	44.9	2.35	40.1	1.66
		Anolyte	4	53.1	—	1.21	44.9	3.20	32.1	1.34
II	Run 4	Catholyte	4	50.4	0.5	2.91	14.9	2.65	58.4	1.13
		Anolyte	4	52.9	—	0.38	14.9	3.41	50.8	0.43
	Run 5	Catholyte	4	50.4	0.5	2.88	29.9	2.20	55.6	0.97
		Anolyte	4	52.9	—	0.38	29.9	3.12	43.4	0.43

Supporting Electrolyte Condition (I or II)	Glycerol Conversion (%)	Aqueous Phase Organic Product Selectivity (%) ^[1]								Carbon Balance (%)	Faradaic Efficiency (%)		
		C ₃						C ₂				C ₁	
		GLAD	DHA	GLA	HPA	GAD	GA	GLOA	FA				
I	Run 1	Catholyte	18.8	47.8	19.1	2.6	—	10.1	3.7	0.5	12.0	99.2	69.1
		Anolyte	18.9	43.1	6.6	37.9	0.7	—	3.6	—	0.3	98.5	71.2
	Run 2	Catholyte	38.0	37.1	15.9	4.0	—	7.9	4.1	0.7	11.9	93.0	63.8
		Anolyte	37.8	32.3	5.2	35.4	1.0	—	3.7	—	0.4	91.7	63.1
	Run 3	Catholyte	53.3	29.5	13.9	4.7	—	8.4	5.9	2.1	15.9	89.5	68.4
		Anolyte	51.6	29.4	5.8	40.9	1.4	—	4.7	—	0.4	91.0	63.3
II	Run 4	Catholyte	23.2	33.2	10.3	1.8	0.3	7.5	2.5	1.0	9.1	92.0	61.7
		Anolyte	18.1	44.3	8.3	38.1	0.4	—	3.9	—	0.3	99.2	70.0
	Run 5	Catholyte	39.3	25.4	9.4	2.9	1.4	7.2	4.3	1.5	14.1	86.7	64.0
		Anolyte	35.9	32.7	5.7	40.0	0.5	—	5.0	—	0.3	94.3	65.4

^[1] GLAD = glyceraldehyde; DHA = dihydroxyacetone; GLA = glyceric acid; HPA = hydroxypyruvic acid; GAD = glycolaldehyde; GA = glycolic acid; GLOA = glyoxylic acid; FA = formic acid.

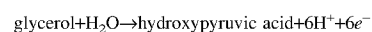
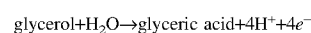
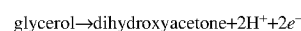
[0164] Here we provide the details in the Faradaic efficiency (FE) calculation for glycerol valorization at the NiSe₂ cathode and the Pt anode.

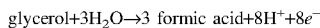
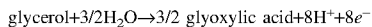
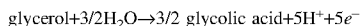
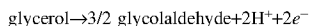
[0165] The FE of all detected aqueous phase organic products (i.e., not including the potential product of CO₂, which is not detectable by ¹H NMR) from glycerol oxidation at the Pt anode (FE_{anode}) can be calculated using the following equation:

$$FE_{anode}(\%) = \frac{\sum_{n=1}^3 \left\{ \frac{n}{3} \times [C_n \text{ product}]_f \times V_f \times x \times F \right\}}{Q_{total}} \times 100\%$$

where V_f is the final electrolyte volume, [C_n product]_f is the final concentration of C_n product (n=1, 2, 3), x is the

theoretical number of electrons transferred for oxidizing 1 molecule of glycerol to 3/n molecule(s) of a specific C_n product at anode (x=2 for glyceraldehyde, dihydroxyacetone, or glycolaldehyde; x=4 for glyceric acid; x=5 for glycolic acid; x=6 for hydroxypyruvic acid; x=8 for glyoxylic acid, or formic acid) based on the balanced anodic half-cell reactions below (see FIG. 4b), F is the Faraday constant (96485 C mol⁻¹), Q_{total} is the total amount of charge passed.

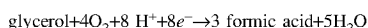
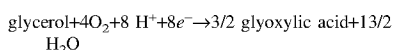
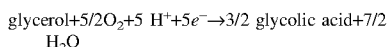
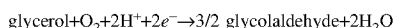
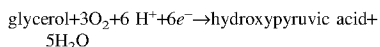
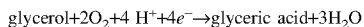
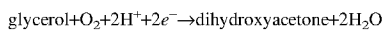
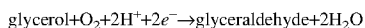




[0166] The calculated FE_{anode} values for the anodic half-cell studies (63-85%) and the linear paired experiments (63-71%) are listed in Table 3 and 5, respectively. These calculated FE_{anode} values are less than unity due to the oxidation of formic acid into CO_2 at the Pt anode. An earlier literature also showed the possible formation of CO_2 from glycerol oxidation at Pt anode under similar applied potential and pH conditions.

[0167] On the other hand, the estimate of the FE for the cathodic electro-Fenton process is complicated by the multi-step process. We assume that cathodic valorization of glycerol theoretically proceeds via electrogeneration of H_2O_2 from O_2 ($\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$), followed by using H_2O_2 as the oxygen source that is using the $\cdot\text{OH}$ and Fe^{3+} pair generated from the Fenton reaction ($\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot\text{OH} + \text{OH}^-$) as the oxidants to oxidize glycerol in the solution.

[0168] The balanced cathodic half-cell reactions should theoretically be (see FIG. 4a):



[0169] The FE of all detected aqueous phase organic products from glycerol valorization at the NiSe_2 cathode ($FE_{cathode}$) can be estimated using the following equation:

$$FE_{cathode}(\%) = \frac{\sum_{n=1}^3 \left\{ \frac{n}{3} \times [C_n \text{ product}]_f \times V_f \times y \times F \right\}}{Q_{total}} \times 100\%$$

where y is the theoretical number of electrons transferred for oxidizing 1 molecule of glycerol to $3/n$ molecule(s) of a specific C_n product ($n=1, 2, 3$) at cathode as shown in the balanced cathodic half-cell reactions above ($y=2$ for glycerolaldehyde, dihydroxyacetone, or glycolaldehyde; $y=4$ for glyceric acid; $y=5$ for glycolic acid; $y=6$ for hydroxypyruvic acid; $y=8$ for glyoxylic acid, or formic acid). Note that this would be a conservative lower bound estimate of the $FE_{cathode}$, because any non-ideal electro-Fenton process will lead to larger y values and thus larger $FE_{cathode}$ values. The estimated $FE_{cathode}$ values for the cathodic half-cell studies (52-58% when $[\text{Fe}^{2+}] = 0.5 \text{ mM}$) and the linear paired experiments (62-69% when $[\text{Fe}^{2+}] = 0.5 \text{ mM}$) are listed in Table 3

and 5, respectively. These estimated $FE_{cathode}$ values are less than unity due to the oxidation of formic acid into CO_2 at the NiSe_2 cathode.

Example 2

[0170] Synthesis and Characterization of PdSe_2 Nanoplates. We synthesized layered PdSe_2 (FIG. 32a) using a facile hydrothermal reaction by reacting palladium chloride and selenourea in near-stoichiometric amounts. PdSe_2 nanoplates with similar morphology (and variable thickness/size) could also be prepared by liquid exfoliation from bulk PdSe_2 crystals. The powder X-ray diffraction pattern (PXRD) of as-synthesized PdSe_2 matched the standard pattern (FIG. 32b) without detectable impurities from other known Pd—Se phases. Scanning electron microscopy (SEM) images show that the resulting PdSe_2 has a nanoplate-like morphology, with enriched surface area in the (200) basal plane compared to the (002) edges (FIG. 32c). The Raman spectra (FIG. 32d) matched the previously reported spectrum for bulk PdSe_2 , suggesting the as-prepared PdSe_2 nanoplates do not approach few-layer thicknesses. To elucidate the electronic structure of PdSe_2 , we then conducted X-ray absorption near edge spectroscopy (XANES) at the Pd L_3 -edge (FIG. 32e), wherein the position of the white line and the white line intensity were most similar to that of PdO (Pd^{2+}), falling between the intensities/edge positions of Pd foil (Pd^0) and K_2PdCl_6 (Pd^{4+}), suggesting that the Pd sites in PdSe_2 have a near 2+ oxidation state. Se K-edge XANES showed similarity in XANES peak shapes to Se_2^{2-} compounds, such as CoSe_2 , which has similar Se—Se dumbbells. Pd L_1 and L_2 edge XANES further supported a Pd^{2+} oxidation state.

[0171] Evaluation of the 2e^- ORR Activity, Selectivity and Operational Stability of PdSe_2 . To evaluate the 2e^- ORR activity, selectivity, and stability of PdSe_2 , electrochemical tests using a rotating ring disk electrode (RRDE) in acidic (0.05 M H_2SO_4 , pH=1.2) and neutral (0.05 M NaPi buffer=0.025 M $\text{Na}_2\text{HPO}_4/0.025 \text{ M NaH}_2\text{PO}_4$, pH=6.5) conditions (FIG. 33a) were conducted. In contrast to other metal compound electrocatalysts, the activity of PdSe_2 in buffered neutral conditions is higher than its activity in acidic conditions, while high selectivity ($\geq 80\%$) is maintained in both pH conditions at potentials up to 0.05 V vs. RHE. The RRDE results for PdSe_2 suggest that PdSe_2 can produce large amounts of H_2O_2 while operating at higher overpotentials, compared to other electrocatalysts measured in neutral solution (FIG. 33b) which primarily have large partial kinetic current towards H_2O_2 production ($j_{k,peroxide}$) at lower overpotentials, but decrease in current at higher overpotentials (more cathodic). Furthermore, the RRDE measurements of Pd^{4+}Se and $\text{Pd}_{17}\text{Se}_{15}$ further highlight the unique behavior of PdSe_2 in the family of Pd—Se phases, with only PdSe_2 exhibiting high selectivity and activity for H_2O_2 production. The stability of the PdSe_2 phase was further evaluated at a fixed potential of 0 V vs. RHE over >6 hours while continually monitoring the ring current and consequent H_2O_2 selectivity (FIG. 33c). The ring current remained $>1 \text{ mA/cm}^2_{disk}$ for the duration of the measurement, indicating that $>80\%$ selectivity can be continuously maintained. However, some decrease in the disk current was observed over time, which could indicate some changes occurring at the catalyst that even further increase the barrier to the 4e^- pathway.

[0172] Bulk Electrosynthesis of H_2O_2 on PdSe_2 . To evaluate the practical performance of PdSe_2 for electrosynthesis

of H_2O_2 , Inventors prepared a gas diffusion electrode (GDE) loaded with PdSe_2 catalyst (FIG. 39a) and applied a pulsed electrolysis procedure in a two-compartment flow cell to rapidly accumulate H_2O_2 (see Methods). Inventors initially measured CV on the PdSe_2/GDE electrode and observed a cathodic current onset of ~ 0.6 V vs. RHE, and a large increasing current up to almost -90 mA (or -16 mA cm^{-2}) at 0 V vs. RHE (FIG. 39b).

[0173] Based on the CV, Inventors performed an extended electrosynthesis test at a fixed current of -30 mA (FIG. 39c). After an initial onset curve, the potential remained fairly constant at ~ 0.3 V vs. RHE over a 3-hour electrolysis, and yielded an accumulated H_2O_2 concentration of 870 ppm (FIG. 39d). Rapid accumulation of H_2O_2 was also achieved over the PdSe_2/GDE electrode at constant currents of -85 mA and -60 mA (FIG. 39c,d) allowing for accumulation of a similar amount of H_2O_2 (785 ppm) in just 15 minutes with a Faradaic efficiency of $>50\%$ and a potential of ~ 0 V vs. RHE. After the electrosynthesis, the final pH remained near neutral for all measurements.

[0174] The drops in Faradaic efficiency over the duration of bulk electrolysis are similar to that observed for cubic NiSe_2 . To understand this, Inventors comprehensively considered both the production and decomposition of the H_2O_2 and also computationally compare the expected catalytic properties of 2D pentagonal PdSe_2 against those of pyrite phase NiSe_2 with a cubic symmetry and identical (100) and (001) surfaces (FIG. 1b). NiSe_2 is predicted to be more active than the PdSe_2 based on the stability of OOH^* . The PdSe_2 (100), PdSe_2 (001), and NiSe_2 surfaces each have large barriers for the thermal bond dissociation of OOH^* [reaction (7)], which is beneficial for $2e^-$ ORR. Since both PdSe_2 (100)/(001) and NiSe_2 show barrierless PCET steps for $2e^-$ ORR with larger barriers for reaction (4), both should favor $2e^-$ ORR over $4e^-$ ORR. However, the barrier for the further reduction of H_2O_2 [reaction (5)] over NiSe_2 lies between those of PdSe_2 (100) and PdSe_2 (001) surfaces, which can be explained by the trend of the relative stability of OH^* to H_2O_2^* (or the Brønsted-Evans-Polanyi (BEP) principle). Therefore, the PdSe_2 (001) surface is expected to demonstrate better selectivity and accumulation of H_2O_2 , and the kinetic behavior of NiSe_2 and PdSe_2 (100) edges may dictate the overall Faradaic efficiency of electrosynthesis over these surfaces.

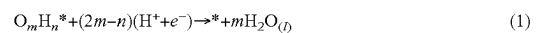
[0175] Notably, the PdSe_2/GDE electrosynthesis performance is dependent on the loading and morphology of the deposited catalyst film—a PdSe_2 film with higher loading on the GDE limited the Faradaic efficiency and accumulation of H_2O_2 during electrolysis. This was most likely due to inhibited O_2 transport to the triple phase boundary. Despite this, all GDE flow cell electrosyntheses resulted in significantly more H_2O_2 accumulation in a much shorter time than a traditional H-cell electrosynthesis, which highlights the importance of cell design in evaluating the performance of $2e^-$ ORR catalysts. The high H_2O_2 production rate (7933 mmol $\text{g}_{\text{catalyst}}^{-1} \text{h}^{-1}$) at 0 V vs. RHE is notably among the highest to reach practically useful concentrations of H_2O_2 in a conventional flow cell device.

[0176] Post-Electrolysis and Operando Stability of PdSe_2 . In order to confirm the predicted stability of PdSe_2 experimentally, several post-electrolysis experiments were conducted. First, in order to evaluate PdSe_2 's viability for direct applications where only small amounts of Pd and Se leaching into solution can be tolerated (i.e. wastewater treatment,

semiconductor cleaning), we measured the amount of Pd and Se leached during electrolysis at 0.2 V vs. RHE and 0.3 V vs. RHE using inductively coupled plasma optical emission spectroscopy (ICP-OES) and found that Pd leaching was near-zero at the more active operating potential of 0.2 V vs. RHE, while Se leaching increased at the more active $2e^-$ ORR potential (FIG. 35a). The effective amount of Se in the low-volume (<5 mL) H-cell is slightly higher than the allowed amount in drinking water, this problem could likely be solved by operating $2e^-$ ORR on PdSe_2 in high volume flow-cell devices. Despite this small amount of metal leaching, there was very little change observed in the Raman spectrum (FIG. 35b) and the XRD pattern (FIG. 35c) of the catalyst after the electrolysis, indicating that the bulk structure of PdSe_2 is maintained after the electrolysis. Similarly, X-ray photoelectron spectroscopy (XPS) indicated that the electronic environment of Se changed little before and after the electrolysis (FIG. 35d), indicating that the O^* adsorption, which prefers the Se site, did not permanently modify the Se on the surface after operation. However, the Se/Pd ratio increased post-operation, suggesting that the leaching could trigger some surface rearrangement.

[0177] After confirming ex-situ that the PdSe_2 maintained its bulk structure and surface electronic environment before and after electrolysis, we sought to probe the dynamic electronic and local structure environments during the true operating conditions of PdSe_2 during $2e^-$ ORR using operando XAS. Interestingly, the Se K-edge XANES peak shape and edge position were unchanged from E_{OC} up to potentials of 0 V vs. RHE (FIG. 35e). The lack of changes in the intensity of the white line or edge position indicates that there is no substantial adsorption of oxygenates on the Se sites. Similarly, the extended Se K-edge X-ray absorption fine structure (EXAFS) spectra at the same set of potentials are completely overlapped (FIG. 35f). Thus, the average local environment around the Se must remain unchanged, further indicating no substantial absorption oxygenates are generated during the $2e^-$ ORR process. In contrast, the Pd K-edge spectrum does show small shifts in the XANES as well as minor coordination changes in the EXAFS, which is a result of oxygenate adsorption slightly changing the electronic environment and local structure around the Pd sites.

[0178] Surface Pourbaix Diagrams. To understand the electrochemical stability of PdSe_2 , we calculated the surface Pourbaix diagrams of the (001) and (100) surfaces under the assumption that the surfaces are in equilibrium with bulk water. The proton-coupled electron transfer (PCET) reaction of a general adsorbate can be written as:



The electrochemical potentials of a proton and an electron pair were calculated by using the computational hydrogen electrode (CHE) method (Equation 2).

$$\widetilde{\mu}_{\text{H}^+} + \widetilde{\mu}_{e^-} = 0.5\mu_{\text{H}_2} - U_{\text{RHE}} \quad (2)$$

where $\widetilde{\mu}_{\text{H}^+}$ and $\widetilde{\mu}_{e^-}$ are electrochemical potentials of a proton and an electron, and μ_{H_2} is a chemical potential of hydrogen gas at the standard state, and U_{RHE} refers to the applied potential vs RHE. The preferential binding sites for H, O, OH and OOH on two surfaces are shown in Table 6.

TABLE 6

The preferential binding sites for O*/OH*/OOH* on (001) and (100) surfaces of PdSe ₂ . Note that OOH is assumed to have no preferential binding site on (001) because the difference in adsorption energy is less than 0.05 eV.		
	(001)	(100)
H*	Se	Pd
O*	Se	Se
OH*	Se	Pd
OOH*	—	Pd

[0179] Clean surface is predicted for the (001) surface over a wide range of potential, which is unsurprising considering its small surface energy, indicating that this surface is much more stable than the (100) surface. Likewise, (100) surface is predicted to be bare at the applied potential although the potential window where the clean surface is predicted is narrower. Note that bond breaking is not required to generate the (001) surface because the interaction between layers is through the van der Waals interaction. Pd atoms on the (001) surface have the same coordination number as that of bulk Pd atoms. Although the coordination number of Se atoms does not change, Se atoms of bulk PdSe₂ will interact with the atoms in a neighboring layer. This will make Pd atoms on the (001) surface less active. On the other hand, Pd—Se bonds need to be broken to generate the (100) surface, which makes this surface more reactive. Because the implicit solvation model, such as VASPsol, cannot describe the competitive water adsorption, the interaction of water with PdSe₂ should be taken into account, considering water adsorption energy on the (100) surface is strong and the preferential binding sites for H₂O and OOH are the same. To investigate if all the Pd atoms are covered by specifically adsorbed water or not, ab-initio molecular dynamics (AIMD) was performed over 10 picoseconds by putting 30 water molecules in the 2×1 supercell of the PdSe₂ (100) slab and we found that the specifically adsorbed water will occupy half of Pd atoms of the (100) surface and this can affect the adsorption energies of adsorbates, such as O*, OH*, OOH* and H*. After equilibration steps, 2 Pd atoms out of 4 Pd atoms are always covered, and desorption did not occur during AIMD. This AIMD result is consistent with the calculations along with VASPsol, which shows that the adsorption free energy of 0.5 ML (monolayer) gives -0.54 eV while that of 1.0 ML is -0.58 eV, i.e., the differential adsorption free energy from 0.5 ML to 1.0 ML is small enough (-0.04 eV) that the thermal fluctuation can overcome. Therefore, for the (100) surface, we put 1 specifically adsorbed water molecule on Pd for all configurations. Note that both give the clean surface at the applied potential although the presence of a specifically adsorbed water molecule makes the surface more stable.

[0180] Free energy diagrams. We further calculated the free energy diagrams of 2e⁻ ORR to investigate the activity and selectivity of the PdSe₂ catalyst. Likewise, two surfaces, (001) and (100), were considered, and the CHE method was utilized to treat the electrochemical potential of a proton/electron pair. Note that there is one specifically adsorbed H₂O, which corresponds to 0.5 ML, for the (100) surface. At the calculated equilibrium potential of 2e⁻ ORR, the first PCET step is uphill by 0.45 eV and downhill by 0.34 eV on (001) and (100) surfaces, respectively, which is unsurprising considering that the (001) surface is more stable than the

(100) surface, which will lead to making the OOH* state unstable. Note that the corresponding coverage used for the free energy is 0.5 ML and the stability of the OOH* state also depends on its coverage (Table 7).

TABLE 7

The adsorption free energy (in eV) of OOH* on the (001) and (100) surface of PdSe ₂ at various coverages at calculated equilibrium potential. The coverage used in the free energy diagrams corresponds to 0.500 ML.		
OOH* Coverage (ML)	(001)	(100)
0.125	0.47	
0.250	—	
0.500	0.45	-0.34
1.00	0.48	-0.34

TABLE 8

Activation barriers of thermal bond dissociation steps (eV).		
	(100) facet	(001) facet
O—O	1.04	0.77
O—OH	0.66	0.74
HO—OH	0.58	0.24

[0181] Considering that the standard reduction potential of 4e⁻ ORR (1.23 V) is higher than that of 2e⁻ ORR (0.69 V), kinetics should be taken into account to explain the selectivity. Because the adsorbates are likely to result in 4e⁻ ORR once the O—O bond is broken, we considered three thermal bond dissociation processes:



Although all these steps are thermodynamically favorable, all the activation barriers are much higher than that of the O—OH bond breaking on Pd metal (0.06 eV), suggesting that the high activation barriers can stem from the spatial separation of active sites, which will result in the high selectivity for 2e⁻ ORR. Note that the activation free energy of the bond dissociation of hydrogen peroxide on the (100) surface is relatively small (0.24 eV), but this activation energy can be high considering the competing step is desorption from the surface, which is assumed to be barrierless.

[0182] Kinetics of PCET. In addition to thermal bond dissociation steps, we considered relevant PCET processes to investigate the selectivity for 2e⁻ ORR:



To obtain activation energy for an electrochemical process, a solvated proton should be treated explicitly unlike the CHE method. Among several models for a solvated proton, such as a Zundel ion (H₅O₂⁺), the Eigen ion (H₃O₄⁺) and the water bilayer model, we used the Eigen ion as a proton donor

because the use of the Eigen ion was validated for HER on Pt. Furthermore, because the purpose of this calculation lies in the comparison of activation energy, we believe it is safe to rely on the static minimum energy path and ignore the entropic effects and solvent fluctuations. In addition, we believe the trend remains the same even if the proton donor changes from a solvated proton to water. To obtain constant-potential activation barriers, the number of electrons varied so that the work function, which is related to electrode potential, is fixed. The details about this methodology can be found in *J. Phys. Chem. C* 2019, 123, 4116–4124, incorporated by reference, for any purpose, herein.

[0183] By using the nudged elastic band (NEB) method and the dimer method, we calculated the “raw” activation energy. The raw activation energy means the work function varies across the reaction. First, the most important step to determine the selectivity for $2e^-$ ORR is the second PCET step (Equations 7 or 8). On the (100) surface, the step of reducing OOH to H_2O_2 is a barrierless step (the raw activation barrier is zero), while the step of reducing OOH to $H_2O_{(l)}+O^*$ gives a barrier of 0.44 eV. By varying the number of electrons to set the electrode potential to be -0.21 V vs SHE, which corresponds to 0.2 V vs RHE at pH 7 and constant, the potential constant activation barrier becomes 0.37 eV, i.e., the potential-constant correction term is small. This is because the change in work function is small enough and the work function is already close to the target potential. Thus, it is sufficient to consider just the “raw” activation energy to compare competing reaction steps. Similarly, others have shown that the constant potential correction term is sufficiently small, they used the average value of the potential at the initial and final states. This is particularly important for the (001) surface because there are some issues, such as a non-zero band gap and dependence of the potential of zero charge (PZC) on the interlayer distance, that make it tricky to convert raw activation barriers into potential-constant activation barriers.

[0184] Similarly, on the (001) surface, the step of reducing OOH to H_2O_2 becomes barrierless, while that of reducing OOH to $H_2O_{(l)}+O^*$ has a barrier of 0.23 eV. Therefore, the high selectivity for $2e^-$ ORR can be explained by kinetics.

[0185] Additionally, we calculated the activation barrier for other steps (Equations 6 and 9). Because the further reduction of H_2O_2 shows a larger activation barrier than that of the first PCET step, this can explain the selectivity of H_2O_2 production.

[0186] pH dependence of the activity. The pH dependence of the activity of electrochemical processes like ORR has been explained by the stabilization of the OOH* state, which arises from the interaction with the electric field formed at the interface when the applied potential deviates from the PZC. Note that the OOH* state is calculated at PZC in the CHE method and the potential dependence is added as a posteriori correction via the RHE scale, where the applied potential is coupled with pH. Therefore, to decouple the electrode potential and pH, we calculated the binding energy of OOH* including the interaction of OOH with the electric field formed at the interface because the electric field formed at the interface is related to the shift in potential from the PZC (Equation 1). Others calculated the dipole moment and polarizability of each adsorbate by fitting a second-order polynomial (Equation 2) to calculations across the range of external electric fields and concluded that OOH* becomes stable as pH decreases.

$$\vec{E} = \frac{C_{dl}(U_{SHE} - U_{PZC})}{\epsilon\epsilon_0} \quad (10)$$

$$G_{ads} = G_{ads}^{PZC} + \mu\vec{E} - \frac{1}{2}\alpha\vec{E}^2 \quad (11)$$

[0187] In the same manner, we calculated the dipole moment and polarizability of OOH* by applying the external electric field from -0.6 V/Å to 0.6 V/Å. (FIG. 38) The PZC (0.2 V vs SHE) and the double layer capacitance (13.6 $\mu\text{F}/\text{cm}^2$) of the PdSe₂ catalyst was calculated by adding/removing electrons and measuring the work functions. As mentioned above, because the PZC of (001) surface is highly sensitive to the distance between slabs and few-layers slab has a non-zero band gap, we used the values from (100) surface for both surfaces. The absolute electrode potential deviates more from its PZC as pH increases by 0.06^*pH , leading to an increase in the magnitude of the electric field formed at the interface, which helps stabilize the OOH* by 0.1 eV at pH 6.5 on the (001) surface. The stability of the OOH* shows a different trend depending on the facet; the OOH* state on the (001) facet is uphill at the calculated equilibrium potential, while it is downhill on the (100) surface. Stabilization will lead to an increase in the activity for $2e^-$ ORR.

[0188] Regarding the (100) surface, the presence of specifically adsorbed water and the adsorption decrease as pH increases, i.e., it is more likely that O₂ can replace the adsorbed water at high pH.

[0189] Ex-situ and In-situ Studies on the Stability of PdSe₂. To confirm the predicted stability of PdSe₂, Inventors conducted several post-electrolysis characterization experiments. First, in order to evaluate the viability for direct applications of the produced H_2O_2 where the amounts of metal and Se leaching must be low (i.e. wastewater treatment, semiconductor cleaning), Inventors used inductively coupled plasma optical emission spectroscopy (ICP-OES) to measure the amount of Pd and Se leached into the electrolytes during GDE electrosynthesis conducted with applied constant currents of -30 mA, and -60 mA, and -85 mA (FIG. 35a). The leaching of Pd into the solution from the PdSe₂ catalyst was negligible at all measured operating currents, but the leaching rate increased with increasing current density from 0.05 ± 0.05 $\mu\text{g g}_{cat}^{-1} \text{h}^{-1}$ at -30 mA to 0.5 ± 0.5 $\mu\text{g g}_{cat}^{-1} \text{h}^{-1}$ at -85 mA. The Se leaching rate at an operating current of -30 mA (12.4 ± 0.5 $\mu\text{g g}_{cat}^{-1} \text{h}^{-1}$) was higher than that of Pd and was only slightly higher than the leaching rate of Se from NiSe₂ measured in an H-cell (9.9 $\mu\text{g g}_{cat}^{-1} \text{h}^{-1}$).⁴ Additionally, Inventors compared several other metrics of stability under different operating currents across metal chalcogenide catalysts. One such stability metric is an adaption of the “stability number” (S-number) previously defined for OER catalysts, which we define as the molar ratio of the produced H_2O_2 to leached metal or Se. Inventors find that PdSe₂ has a higher metal S-number than NiSe₂ (~ 105 vs. ~ 103) and PdSe₂ and NiSe₂ have Se S-numbers on the same order of magnitude (~ 600 to ~ 900 depending on conditions).

[0190] Inventors then investigated the chemical stability of the PdSe₂ catalyst. Very little change was observed in the post-electrolysis Raman spectrum (FIG. 35b), showing that the catalyst surface structure is largely maintained. Given the previously observed dependence of the Raman spectrum on PdSe₂ layer number, this also suggests that PdSe₂ does

not significantly delaminate. The XRD pattern of the PdSe₂/GDE after the electrolysis and rinsing with nanopure water closely matched a combination of the XRD patterns of PdSe₂ and the bare GDE (FIG. 35c). X-ray photoelectron spectroscopy (XPS) indicated that the valence states of Pd (FIG. 35d) remained unchanged, suggesting that the Pd²⁺ active sites maintained their surface electronic environment. While there were minor changes to the Se XPS, these changes did not suggest formation of SeO₂, which was observed for other metal chalcogenides. Furthermore, the peak shifts of the Pd 3d and Se 3d XPS due to partial oxidation of PdSe₂ were not observed. Similarly, the Pd—O bond was not observed in the extended Raman spectrum for both pristine PdSe₂ powder and the post-electrosynthesis PdSe₂/GDE electrode. The XPS measurements revealed the Se:Pd ratio decreased post-electrolysis, but was still in excess of a 2:1 ratio, thus precluding the formation of Pd_{1.7}Se_{1.5} triggered by Se leaching. These results confirm that the active site for 2e⁻ ORR is indeed the square planar Pd²⁺ motif, rather than the higher valent Pd or Pd—O bonds formed due to oxidation, as observed for other 2e⁻ ORR catalysts.

[0191] To further investigate the changes to the electronic structure of Se, inventors conducted ex-situ X-ray absorption spectroscopy (XANES) at the Se K-edge. The similar ratio between the main white line peak and the post-white line peak (at ~12660 eV and ~12770 eV) confirms that Se remains anionic in character and precludes the formation of bulk Se oxides. Namely, the peak near 12770 eV was still clearly present, unlike in Se(0) powder, and cationic Se compounds (such as SeO₂) which show a clearly blue shifted white line peak. Additionally, the Se K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy of post-electrosynthesis PdSe₂/GDE showed little change in the first two major peaks (FIG. 35f). Fitting the EXAFS data suggested a minimal decrease in Se—Se coordination (from 1 to 0.8±0.1) but larger decreases in direct Se—Pd coordination (from 2 to 1.0±0.1) and Se—Pd inter-layer coordination (from 1 to 0.3±0.1). Similar results were achieved with a simplified fitting model. Given the Se-rich samples and the lack of significant Pd leaching, these changes in Se—Pd paths could be indicative of some subtle local restructuring of the Pd sites that does not disrupt the overall layered motif of the PdSe₂ catalyst.

[0192] To confirm these stability trends on a longer timescale, we fabricated an electrode with a high loading of Nafion to prevent flooding (FIG. 40a). By tuning the microenvironment, the PdSe₂/GDE electrode was able to operate for 48 hours at -75 mA (FIG. 40b). Additionally, despite the long operation time, the PdSe₂/GDE retained high S-numbers of 416 for Se and 2.07×10⁴ for Pd. The lack of significant decrease in stability at high operating times suggests that H₂O₂ concentration buildup is likely the primary mechanism of Se leaching for PdSe₂. Although the H₂O₂ saturation saturates, the stability is promising for the repeated use of the PdSe₂ catalysts in separate solutions or in a single pass flow cell configuration. After several tests, this electrode was digested for measurement by ICP-OES, which showed a slight decrease from 1.98:1 Se:Pd ratio (as measured in the pristine electrode) to 1.30:1. Taken with the more surface sensitive XPS/EDS results and the bulk sensitive EXAFS, this further suggests differences between the active phase surface and the bulk triggered by Se loss.

Methods and Materials

[0193] Computational Methods. The Vienna Ab initio Simulation Package (VASP) interfaced with the Atomic Simulation Environment (ASE) was used for energies and geometries for all adsorbates. The core electrons are described by projector augmented wave (PAW) pseudopotentials and the Perdue-Burke-Ernzerhof (PBE) functional was used to treat exchange and correlation. Because PBE-TS (Tkatchenko-Scheffler) method gives reasonable lattice constants of bulk PdSe₂, the Tkatchenko-Scheffler method was utilized to treat dispersion. Solvation effects are described by using the implicit solvation model, VASPsol. For numerical stability, the effective surface tension is set to zero, which is validated by the fact that the difference in adsorption energy between the default value (0.025 meV/Å²) and 0 meV/Å² is less than 0.01 eV.

[0194] The Brillouin zone was sampled using 10×10×10, 10×10×1, and 10×8×1 Γ-centered Monkhorst-Pack mesh for bulk, (001), and (100) facets calculations, respectively. When larger supercells were used, the corresponding Brillouin zones were sampled.

[0195] The (001) surface of PdSe₂ was modeled as a 3-layer 1×1 unit cell slab with two bottom layers fixed, which corresponds to 6 Pd atoms and 12 Se atoms. The (100) surface was modeled as 5-layer 1×1 unit cell slab with two bottom layers fixed, which corresponds to 20 Pd atoms and 40 Se atoms. For the electrochemical activation barrier calculations, 4-layer (100) surface was used for efficiency.

[0196] Each electronic self-consistent field (SCF) calculation was converged below 10⁻⁵ eV and the surface adsorbates were allowed to relax until forces became below 0.01 eV/Å. Transition states for thermal bond dissociation were searched using the nudged elastic band (NEB) method and the dimer method. Additionally, all transition states were confirmed first-order saddle points with one imaginary frequency. The free energy of H₂O_(l) was calculated using the experimental free energy difference between H₂O_(l) and H₂O_(g). The free energy of O₂ was determined by setting it to give the experimental standard reduction potential (1.229 V) of the reaction, 0.5 O_{2(g)}+H₂→H₂O_(l). The free energies of adsorbates were calculated using G=E_{DFT}+U_{thermal}+ZPE-TS, where E_{DFT} is the energy obtained from DFT calculation, U_{thermal}, ZPE and S are the contribution from thermal internal energy, the zero-point energy, and entropy, which are calculated under the harmonic approximation. The free energies of gas-phase/aqueous species, such as H₂, H₂O, and H₂O₂ are calculated by using Gaussian 16 with the SMD continuum solvation model. The calculated standard reduction potential of 2e⁻ ORR is 0.83 V, which is slightly higher than the experimental value (0.69 V) and close to other computed values.

[0197] For potential-constant electrochemical barrier calculations, we included the correction term QV_{ref} which comes from using the finite height of the system, where Q is the net charge of the DFT subsystem and V_{ref} is the negative of the electrochemical potential of the bulk electrolyte. Note that specifically adsorbed water is not considered for the calculations of transition states. Chemicals and materials. Palladium chloride (≥99.9%) was obtained from Sigma-Aldrich. Selenourea (98+%) was obtained from Acros Organics. Carbon fiber paper (CFP, Toray: 5% wet proofing) was obtained from Fuel Cell Earth and plasma treated and briefly heated at 700° C. for 5 minutes prior to

use. Sigracet 28 BC gas diffusion electrodes (GDE) were used for all GDE electro-synthesis measurements.

[0198] Materials synthesis. The PdSe₂ nanoplates were synthesized by a hydrothermal method. Briefly, 1.0 mmol of PdCl₂ (0.18 g) and 2.0 mmol selenourea (0.25 g) were dissolved in 9 mL of nanopure water and added to a Teflon lined 20 mL stainless steel autoclave. A piece of CFP (~1.8 cm×~2.2 cm) was also added to the autoclave. The autoclave was sealed and heated at 220° C. for 12 hours, and then cooled naturally in air. The resulting powder was washed with nanopure water and ethanol before being dried under vacuum at 60° C., and the CFP piece was similarly rinsed with nanopure water and ethanol and then dried in air. Nanoparticles of Pd₄Se and Pd₁₇Se₁₅ were synthesized by similar methods with appropriate stoichiometric amounts of PdCl₂ and selenourea.

[0199] Materials characterization. Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 ADVANCE powder X-ray diffractometer using Cu K α radiation with a 0.6 mm slit. Scanning electron microscopy (SEM) images were collected on a Zeiss SUPRA 55VP field emission scanning electron microscope at an accelerating voltage of 1-3 kV for imaging, and electron dispersive spectroscopy (EDS) spectra were collected on the same microscope using an accelerating voltage of 22 kV and a Thermo Scientific UltraDry EDS Detector. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific K-Alpha XPS system with an Al K α X-ray source. Raman spectra were collected on a Thermo Fisher Scientific DXR3xi Raman Imaging Microscope using a 532 nm laser with a 10 mW laser power. X-ray absorption spectroscopy (XAS) was collected at beamlines 10-ID (Pd K-edge data) and beamline 9-BM (Se K-edge data, Pd L-edge data) of the Advanced Photon Source at Argonne National laboratories in fluorescence mode with an ion chamber detector for the Pd K-edge, a Vortex silicon drift detector for the Pd L-edge, and a Passivated Implanted Planar Silicon (PIPS) detector for the Se K-edge. Pd L-edge spectra were collected in a He-purged sample chamber.

[0200] Rotating ring disk Electrode Preparation. Catalysts were drop-casted onto a rotating ring-disk electrode (RRDE, Gaoss Union, 4 mm disk diameter) which was polished successively with 1, 0.3, and 0.05 μ m alumina suspensions (Allied High Tech Products) on polishing pads (Buehler, MicroCloth), and subsequently rinsed with nanopure water before brief (~20 seconds) sonication in ethanol then quickly blown dry with N₂. Catalyst dispersions typically used a 1:9 v:v mixture of Nafion solution and water with an effective catalyst loading of ~12 μ g/ μ L.

[0201] Rotating ring-disk electrode measurement. RRDE measurements were conducted in an undivided cell using a Bio-Logic VMP3 potentiostat. A graphite rod was used as the counter electrode and a Hg/Hg₂SO₄ reference electrode (CH Instruments Inc., CHI151) that was calibrated against a saturated calomel electrode (CH Instruments Inc., CHI150). The cell contained approximately 45 mL of electrolyte, which was pre-purged with Ar or O₂ gas before measurement, and then the corresponding gas was kept in the headspace of the solution for the duration of the measurement. During RRDE measurements, the ring was typically held at 1.3 V vs. RHE (pre iR correction) where H₂O₂ reduction is diffusion limited. The H₂O₂ selectivity was then calculated according to the follow equation:

$$\text{H}_2\text{O}_2 \text{ Selectivity (\%)} = \frac{200 \left(\frac{I_{\text{ring}}}{N} \right)}{\frac{I_{\text{ring}}}{N} + I_{\text{disk}}}$$

where N is the collection efficiency of the ring, which was calculated using a ferri-/ferrocyanide redox couple.

[0202] Bulk electrolysis measurements. Bulk electrolysis experiments were conducted in a glass H-cell with an Hg/Hg₂SO₄ reference electrode. The working electrode consists of the as-synthesized PdSe₂ catalyst directly grown onto carbon fiber paper (CFP) cut into a 1×2 cm area, where the area exposed to electrolyte was ~1 cm² with the electrode contacted via a Teflon clip with a platinum contact. The other chamber, separated by a Nafion-117 membrane, contained a graphite rod which served as the counter electrode. The working chamber was pre-purged with O₂ and then kept under a continuous flow of O₂ gas during the measurement. Aliquots were continuously taken during the measurement and added to solutions of ~0.4 mM Ce(SO₄)₂, which were then measured shortly thereafter by UV-Vis on a JASCO V-570 UV/Vis/NIR spectrophotometer, which were converted to the corresponding concentration of H₂O₂ via the following equation:

$$\text{Cumulative Faradaic Efficiency} = \frac{Q_{\text{H}_2\text{O}_2}}{Q_{\text{tot}}} = \frac{2 * F * [\text{H}_2\text{O}_2] * V_{\text{tot}}}{Q_{\text{tot}} * 10^6}$$

where F corresponds to Faraday's constant (in C/mol e⁻), [H₂O₂] is the H₂O₂ concentration (in mM) calculated from the previous equation, V_{tot} corresponds the total solution volume (in mL), and Q_{tot} is the total charge passed through the measurement (in C).

$$\text{Cumulative H}_2\text{O}_2 \text{ Selectivity} = \frac{200}{1 + \left(\frac{100}{\text{Cumulative Faradaic Efficiency}} \right)}$$

[0203] Operando X-ray absorption spectroscopy measurements. Operando XAS measurements performed at the Advanced Photon Source were collected using a custom-built fluorescence detection H-cell where the working electrode was mounted on the front using an acrylic or aluminum face plate, with the catalyst side facing inward to the electrolyte and the bare side facing back towards the incident X-rays and the fluorescence detector. To contact the working electrode under the faceplate, a small piece of copper foil was used. A leakless Ag/AgCl reference electrode was used (and secured in the front chamber with the working electrode) and a graphite rod was used as the counter electrode in the back chamber, which was separated from the front chamber by a Nafion-117 membrane to avoid H₂O₂ crossover and decomposition. 2.5 mL of electrolyte was added to the front chamber for each measurement, and was kept under a continuous stream of O₂ gas throughout the duration of the measurement via a port in the top of the cell. XAS spectra were continuously collected for the duration of the measurement, with each displayed spectrum representing the average of at least three raw spectra.

1. An electrochemical cell comprising an electrolyte and a cathode immersed in the electrolyte,

wherein the cathode comprises a two-electron oxygen reduction reaction ($2e^-$ ORR) electrocatalyst composed of a metal chalcogenide,

wherein the metal is Ni or Pd.

2. The electrochemical cell of claim 1, wherein the metal chalcogenide comprises c-NiSe₂.

3. The electrochemical cell of claim 1, wherein the electrolyte has a pH below 4.0, optionally wherein the electrolyte has a pH between 0.0 and 4.0 pH or any pH therebetween.

4. The electrochemical cell of claim 1, wherein the metal chalcogenide comprises layered PdSe₂.

5. The electrochemical cell of claim 1, wherein the electrolyte has a pH above 4.0, optionally wherein the electrolyte has a pH between 4.0 and 8.0 pH or any pH therebetween.

6. The electrochemical cell of claim 1, wherein the electrolyte comprises oxygen (O₂), hydrogen peroxide (H₂O₂), hydroxyl radical (\cdot OH), a regenerable metal ion, and a first biomass-derived feedstock.

7. The electrochemical cell of claim 6 further comprising an acidic anolyte and an anode immersed in the anolyte, wherein the anolyte comprises a second biomass-derived feedstock.

8. A method for production of hydrogen peroxide, the method comprising introducing oxygen into the electrochemical cell according to any one of claim 1 under conditions sufficient for preparing the hydrogen peroxide.

9. An electrochemical cell comprising an acidic catholyte, a cathode immersed in the catholyte, an acidic anolyte, and an anode immersed in the anolyte,

wherein the cathode comprises a two-electron oxygen reduction reaction ($2e^-$ ORR) electrocatalyst comprised of a metal chalcogenide and the catholyte comprises oxygen (O₂), hydrogen peroxide (H₂O₂), hydroxyl radical (\cdot OH), a regenerable metal ion, and a

first biomass-derived feedstock, and wherein the anolyte comprises a second biomass-derived feedstock.

10. The electrochemical cell of claim 9, wherein the two-electron oxygen reduction reaction ($2e^-$ ORR) electrocatalyst comprises a metal chalcogenide.

11. The electrochemical cell of claim 10, wherein the metal chalcogenide comprises an earth-abundant metal or a noble metal.

12. The electrochemical cell of claim 10, wherein the metal chalcogenide comprises Ni, Co, Fe, Cu, Mn, Pd, or any combination thereof.

13. The electrochemical cell of claim 10, wherein the metal chalcogenide comprises c-NiSe₂, PdSe₂, pyrite or marcasite type CoSe₂, pyrite type CoS₂, or CuCO_{2-x}Ni_xS₄.

14. The electrochemical cell of claim 9, wherein the acidic catholyte and/or the acidic anolyte has a pH between 0.0 and 4.0 pH.

15. The electrochemical cell of claim 9, wherein the regenerable metal ion is Fe²⁺.

16. The electrochemical cell of claim 9, wherein each of the catholyte and the anolyte further comprise oxidation products of the first biomass-derived feed stock and the second biomass derived feed stock.

17. A method for preparing an oxidation product of a biomass-derived feedstock, the method comprising introducing the biomass-derived feedstock into the electrochemical cell according to claim 1 under conditions sufficient for preparing the oxidation product.

18. The method of claim 16, wherein a potential between 0.00 and 0.70 V vs. RHE is applied to the cathode.

19. A method for preparing an oxidation product of a biomass-derived feedstock, the method comprising introducing the biomass-derived feedstock into the electrochemical cell according to claim 9 under conditions sufficient for preparing the oxidation product.

20. The method of claim 18, wherein less than 1.0 V of externally applied bias is applied.

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