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(54) Title: BIS-PHENANTHROLINE IRON MACROCYCLE COMPLEX FOR OXYGEN REDUCTION REACTION

(57) Abstract: Disclosed are compounds, compositions, and methods useful for the oxygen reduction reaction (ORR) and capable of operating efficiently at low overpotentials.



***BIS-PHENANTHROLINE IRON MACROCYCLE COMPLEX
FOR OXYGEN REDUCTION REACTION***

RELATED APPLICATIONS

This application claims the benefit of priority to U.S. Provisional Patent Application No. 62/818,284, filed March 14, 2019.

GOVERNMENT SUPPORT

This invention was made with government support under SC0014176 awarded by the Department of Energy. The government has certain rights in the invention.

BACKGROUND

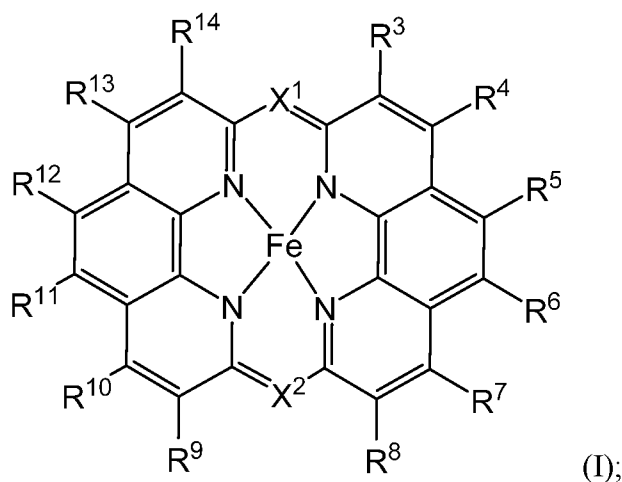
The efficient reduction of molecular oxygen to water is a critical component reaction in many types of fuel cells. Refs. 1,2. Regardless of the fuel source used, the current density output is primarily limited by slow electron transfer rates in the oxygen reduction half reaction at the cathode. Ref. 3. These rates can lag behind the anodic fuel oxidation process by several orders of magnitude thereby urgently motivating the development of improved electrocatalysts for the oxygen reduction reaction (ORR) capable of operating efficiently at low overpotentials. Refs. 4,5. As such, significant effort has been expended developing alternative catalytic materials which are comparably active as Pt-based ORR electrocatalysts at significantly lower cost.

Pyrolyzed iron- and nitrogen-doped (Fe-N-C) materials are leading alternatives to replace Pt-based electrocatalysts. However, developmental progress has been hampered by the fact that the active sites for pyrolyzed catalytic materials remain poorly interrogated. The wide range of preparative procedures found in the literature for the synthesis of doped-graphitic materials has led to uncertainty regarding the identity of the active sites for ORR in these materials. Fe-N-C materials are typically prepared by high temperature pyrolysis of finely dispersed iron salt or porphyrin (refs. 6,7) additives in a MOF (refs. 8,9) or carbon-based support. Refs. 10–12. Much controversy has surrounded the identity of the active sites in pyrolyzed, doped graphitic materials due to the high heterogeneity induced by pyrolysis coupled with a diverse set of synthetic procedures. Metallic iron has been postulated as part of an active site structure (ref. 13) as have various iron-nitrogen coordination environments in an effort to explain X-ray absorption spectroscopy (XAS) results. Refs. 14–17. Numerous reports have corroborated the early assumption that the

ORR active sites are principally iron-containing defects in the hexagonal lattice coordinated by nitrogen atoms. Ref. 18.

SUMMARY

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof:



wherein

X^1 and X^2 are independently N, $C(R^{15})$, $(O^+)X^-$, or $(S^+)X^-$;

X^- is independently for each occurrence boron tetrafluoride, phosphorus tetrafluoride, phosphorus hexafluoride, alkylsulfonate, fluoroalkylsulfonate, arylsulfonate, bis(alkylsulfonyl)amide, bis(fluoroalkylsulfonyl)amide, bis(arylsulfonyl)amide, (fluoroalkylsulfonyl)(fluoroalkylcarbonyl)amide, halide, nitrate, nitrite, sulfate, hydrogensulfate, alkyl sulfate, aryl sulfate, carbonate, bicarbonate, alkyl carboxylate, aryl carboxylate, phosphate, hydrogen phosphate, dihydrogen phosphate, hypochlorite, or an anionic site of a cation-exchange resin;

Y^+ is Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , or $^+NR^{16}R^{17}R^{18}R^{19}$;

R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , and R^{14} are independently hydrogen, halogen, $-CN$, $-OR^{15}$, $-CO_2^-(Y^+)$, $-SO_3H$, $-SO_3^-(Y^+)$, $-NR^{16}R^{17}$, $-NO_2$, substituted or unsubstituted alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl, substituted or unsubstituted heteroaryl, substituted or unsubstituted heterocycloalkyl, haloalkyl, $-OC(O)R^{20}$, $-C(O)R^{20}$, $-C(O)OR^{20}$, $-C(O)NR^{21}R^{22}$, $-S(O)R^{23}$, or $-SO_2R^{23}$; and

R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , R^{20} , R^{21} , R^{22} , and R^{23} are independently hydrogen, haloalkyl,

substituted or unsubstituted alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl, substituted or unsubstituted heteroaryl, or substituted or unsubstituted heterocycloalkyl.

In certain embodiments, X^1 is N; and the compound of Formula I is a Bronsted conjugate acid or a quaternary (C₁-C₆)alkyl ammonium salt at X^1 .

In certain embodiments, X^2 is N; and the compound of Formula I is a Bronsted conjugate acid or a quaternary (C₁-C₆)alkyl ammonium salt at X^2 .

In certain embodiments, X^1 is N; X^2 is N; the compound of Formula I is a Bronsted conjugate acid or a quaternary (C₁-C₆)alkyl ammonium salt at X^1 ; and the compound of Formula I is a Bronsted conjugate acid or a quaternary (C₁-C₆)alkyl ammonium salt at X^2 .

In certain embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein X^1 is C(R¹⁵).

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein X^2 is C(R¹⁵).

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein X^1 is C(R¹⁵); and X^2 is C(R¹⁵).

In other embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein X^1 is N.

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein X^2 is N.

In other embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein X^1 is N; and X^2 is N.

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein X^1 is (O⁺)X⁻ or (S⁺)X⁻.

In certain embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein X^2 is (O⁺)X⁻ or (S⁺)X⁻.

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein X^1 is (O⁺)X⁻ or (S⁺)X⁻; and X^2 is (O⁺)X⁻ or (S⁺)X⁻.

In some embodiments, the disclosure relates to a compound of Formula I or a salt wherein R¹⁵ is hydrogen.

In other embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein R^{15} is substituted or unsubstituted alkyl. Alternatively, R^{15} is substituted or unsubstituted cycloalkyl. In some instances, R^{15} is substituted or unsubstituted aryl. In certain embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein R^{15} is substituted or unsubstituted heteroaryl.

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein at least one of $R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}$, and R^{14} is not hydrogen.

In certain embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein at least two of $R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}$, and R^{14} are not hydrogen.

In other embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein at least three of $R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}$, and R^{14} are not hydrogen.

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein at least four of $R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}$, and R^{14} are not hydrogen.

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein $R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}$, and R^{14} are hydrogen; and X^1 is $C(R^{15})$, $(O^+)X^-$, or $(S^+)X^-$.

In certain embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein $R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}$, and R^{14} are hydrogen; X^1 is $C(R^{15})$, $(O^+)X^-$, or $(S^+)X^-$; and X^2 is $C(R^{15})$, $(O^+)X^-$, or $(S^+)X^-$.

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein $R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}$, and R^{14} are hydrogen; and X^1 is $C(R^{15})$.

In other embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein $R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}$, and R^{14} are hydrogen; X^1 is $C(R^{15})$; and X^2 is $C(R^{15})$.

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein $R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}$, and R^{14} are hydrogen; and X^1

is $(O^+)X^-$ or $(S^+)X^-$.

In certain embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein $R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}$, and R^{14} are hydrogen; X^1 is $(O^+)X^-$ or $(S^+)X^-$; and X^2 is $(O^+)X^-$ or $(S^+)X^-$.

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein $R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}$, and R^{14} are hydrogen; X^1 is N; and X^2 is N.

In some embodiments, the disclosure relates to a composition comprising a compound of Formula I or a salt thereof and a support material; wherein the compound is in contact with the support material.

In certain embodiments, the disclosure relates to a composition wherein the support material comprises carbon. For example, the support material comprises carbon powder. In some instances, the support material comprises carbon black (CB), multi-walled carbon nanotubes (MWCNT), graphene oxide (GO), or reduced graphene oxide (rGO).

In some embodiments, the disclosure relates to a composition wherein the compound is adsorbed on the support material.

In some embodiments, the disclosure relates to a cathode catalyst, comprising a compound of Formula I or a salt thereof or a composition comprising a compound of Formula I or a salt thereof.

In certain embodiments, the disclosure relates to a fuel cell, comprising a cathode catalyst comprising a compound of Formula I or a salt thereof or a composition comprising a compound of Formula I or a salt thereof.

In some embodiments, the disclosure relates to a method of reducing oxygen, comprising:

in an electrochemical device, applying current to a mixture comprising an aqueous medium, hydrogen gas, oxygen gas, and a compound of Formula I or a salt thereof or a composition comprising a compound of Formula I or a salt thereof.

In some embodiments, the disclosure relates to a method of reducing oxygen, wherein the aqueous medium is an alkaline medium.

In certain embodiments, the disclosure relates to a method of reducing oxygen,

wherein the electrochemical device is an anion-exchange membrane fuel cell or an alkaline metal-air battery.

In some embodiments, the disclosure relates to a method of reducing oxygen, wherein the aqueous medium is an acidic medium.

In certain embodiments, the disclosure relates to a method of reducing oxygen, wherein the electrochemical device is a proton-exchange membrane fuel cell.

Other features, objects, and advantages of the invention will be apparent from the detailed description, and from the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 depicts a synthetic route to $(\text{phen}_2\text{N}_2)\text{H}_2$ (compound **5**, also known as phencir H_2) and the Fe(III) complex **6**, $(\text{phen}_2\text{N}_2)\text{FeCl}$.

FIG. 2 depicts optical spectrum of $(\text{phen}_2\text{N}_2)\text{H}_2$ (black, 25 μM in MeCN containing 20 mM trifluoroacetic acid) and $[(\text{phen}_2\text{N}_2)\text{Fe}]^+$ (red, 3.5 μM in MeCN). No optical transitions were observed beyond 800 nm to the instrumentation limit of 1100 nm.

FIG. 3 depicts X-ray absorption near edge structure (XANES) spectra of $(\text{phen}_2\text{N}_2)\text{FeCl}$, reduced $(\text{phen}_2\text{N}_2)\text{FeCl}$, Fe-N-C, reduced Fe-N-C, and OEPFeCl.

FIG. 4 depicts k^2 -weighted Fourier transform of the iron k-edge extended X-ray absorption fine structure spectroscopy (EXAFS) data for $(\text{phen}_2\text{N}_2)\text{FeCl}$, Fe-N-C, and OEPFeCl.

FIG. 5 depicts high resolution N_{1s} X-ray photoelectron spectroscopy (XPS) data of $(\text{phen}_2\text{N}_2)\text{FeCl}$ and Fe-N-C (A); and high resolution Fe_{2p} XPS of $(\text{phen}_2\text{N}_2)\text{FeCl}$ and Fe-N-C (B).

FIG. 6 depicts zero-field ^{57}Fe Mössbauer spectra of $(\text{phen}_2\text{N}_2)\text{FeCl}$ under inert atmosphere at 90 K (A); and zero-field ^{57}Fe Mössbauer spectra of $(\text{phen}_2\text{N}_2)\text{FeCl}$ upon reduction with Cp_2Co under inert atmosphere at 90 K (B).

FIG. 7 depicts cyclic voltammograms of OEPFeCl, $(\text{phen}_2\text{N}_2)\text{FeCl}$ and Fe-N-C inks collected at 5 mV s^{-1} and 2000 RPM in argon-sparged 0.1 M HClO_4 .

FIG. 8 depicts cyclic voltammograms of $(\text{phen}_2\text{N}_2)\text{FeCl}$ /Vulcan/Nafion ink dropcast on glassy carbon disk electrodes in N_2 - and O_2 -saturated (black and red, respectively) 0.1 M HClO_4 aqueous electrolyte collected at 5 mV s^{-1} and 2000 RPM.

FIG. 9 depicts linear sweep voltammograms of (phen₂N₂)FeCl/Vulcan/Nafion (blue), OEPFeCl/Vulcan/Nafion (orange) and Fe-N-C/Nafion (black) inks dropcast on glassy carbon disk electrodes in N₂- and O₂-saturated 0.1 M HClO₄ aqueous electrolyte collected at a scan rate of 5 mV s⁻¹ while being rotated at 2000 RPM. Background carbon ORR activity is given in teal.

FIG. 10 depicts rotating ring-disk electrode voltammogram (ring: red, disk: black) voltammograms of (phen₂N₂)FeCl/Vulcan/Nafion ink dropcast on glassy carbon disk electrodes in O₂-saturated 0.1 M HClO₄ aqueous electrolyte collected at a scan rate of 5 mV s⁻¹ while being rotated at 2000 RPM. The inset displays the onset region.

FIG. 11 depicts number of electrons transferred as a function of potential during ORR catalysis by (phen₂N₂)FeCl/Vulcan/Nafion ink dropcast on glassy carbon disk electrodes in O₂-saturated 0.1 M HClO₄ aqueous electrolyte collected at a scan rate of 5 mV s⁻¹ while being rotated at 2000 RPM.

FIG. 12 depicts (a) Linear sweep voltammograms of Fe-N-C (black), (phen₂N₂)FeCl (blue), OEPFeCl (orange) inks and blank glassy carbon (teal) collected in O₂-sparged 0.1 M NaOH at a rotation rate of 2000 RPM with a scan rate of 5 mV s⁻¹; (b) RRDE plot of (phen₂N₂)FeCl in O₂-sparged 0.1 M NaOH at a rotation rate of 2000 RPM with a scan rate of 5 mV s⁻¹; (c) Number of electrons transferred; and (d) %H₂O₂ produced in base as a function of potential derived from RRDE data for Fe-N-C (black), (phen₂N₂)FeCl (blue) and OEPFeCl (orange).

FIG. 13 depicts voltammograms demonstrating the influence of CO on ORR performance of inks: (a) (phen₂N₂)FeCl in acid, (b) (phen₂N₂)FeCl in base, (c) Fe-N-C in acid, and (d) Fe-N-C in base. Data was collected in either 0.1 M HClO₄ or 0.1 M NaOH at a rotation rate of 2000 RPM and scan rate of 5 mV s⁻¹. Black traces are initial scans in O₂-sparged media, while red data represent scans recorded in O₂- and CO-sparged media. Blue traces were recorded after clearing liquid-phase CO by sparging with O₂.

FIG. 14 depicts voltammograms demonstrating the influence of KCN on ORR performance of inks: (a) (phen₂N₂)FeCl in base and (b) Fe-N-C in base. Data was collected in 0.1 M NaOH at a rotation rate of 2000 RPM and scan rate of 5 mV s⁻¹. Black traces are initial scans in O₂-sparged media, while red data represent scans recorded in O₂-sparged media solution containing 5 mM KCN. Blue traces were recorded after exchanging the electrolyte.

FIG. 15 depicts cyclic voltammogram of 0.25 mM (phen₂N₂)FeCl in Ar-sparged DMF containing 0.52 mM TlOTf, 22 mM [DMF-H][OTf] and 91 mM [TBA][PF₆] collected at a scan rate of 20 mV s⁻¹.

FIG. 16 depicts cyclic voltammograms of 0.5 mM (ph₄phen₂N₂)FeCl in DMF containing ferrocene, 0.1 M [DMF-H][OTf] and 0.1 M [TBA][PF₆]. Under argon atmosphere without 0.1 M LiCl (a), under argon atmosphere with 0.1 M LiCl (b), under argon atmosphere with the same electrolyte as in (b) before introduction of O₂ (c), and under both argon (black) and oxygen atmosphere (red) with the same electrolyte composition as in (b).

FIG. 17 depicts optical spectra of (phen₂N₂)H₂ (black, 26 μM in DMSO) and (phen₂N₂)FeCl (red, 15 μM in DMSO). No optical transitions were observed beyond 800 nm to the instrumentation limit of 1100 nm.

FIG. 18 depicts Zero-field ⁵⁷Fe Mössbauer spectra of Fe-N-C: [D1: (δ = 0.46 mm s⁻¹, |ΔE_Q| = 1.08 mm s⁻¹), D2: (δ = 0.37 mm s⁻¹, |ΔE_Q| = 3.06 mm s⁻¹), top], (phen₂N₂)FeCl: [(δ = 0.39 mm s⁻¹, |ΔE_Q| = 3.06 mm s⁻¹), middle] and [(phen₂N₂)Fe]₂O: [(δ = 0.45 mm s⁻¹, |ΔE_Q| = 0.87 mm s⁻¹), bottom] recorded at 90 K. The spectrum of (phen₂N₂)FeCl was fit to two quadrupole doublets assigned to (phen₂N₂)FeCl (blue) and a residual Fe₂Cl₆•(DMF)₃ impurity [(δ = 0.39 mm s⁻¹, |ΔE_Q| = 1.27 mm s⁻¹), yellow].

FIG. 19 depicts high resolution N 1s and Fe 2p XPS spectra of Fe-N-C (a and e), [(phen₂N₂)Fe]₂O (b and f), [(OEP)Fe]₂O (c and g), and [(Pc)Fe]₂O (d and h).

FIG. 20 depicts XPS high-resolution N 1s spectra of (phen₂N₂)Fe]₂O (top), (phen₂N₂)FeCl (middle) and (phen₂N₂)H₂ (bottom) powders mixed with Au powder and pressed onto conductive carbon tape.

FIG. 21 depicts X-ray absorption spectroscopy data for Fe-N-C (black), [(phen₂N₂)Fe]₂O (blue), [(OEP)Fe]₂O (orange) and [(PcFe)]₂O (aqua). XANES spectra (a), and expanded main-edge region (inset), k²-weighted Fe k-edge EXAFS spectra (b), and k²-weighted Fourier transform Fe EXAFS spectra (c). The energy values of the vertical lines and the alphabetical labels in (a) are taken from reference 15.

FIG. 22 depicts cyclic voltammograms of rotating glassy carbon disk electrodes modified with catalyst films containing Fe-N-C (black), (phen₂N₂)FeCl (blue), (OEP)FeCl (orange), and (Pc)FeCl (aqua). Data were recorded at 5 mV s⁻¹ and 2000 rpm rotation rate in O₂-free 0.1 M HClO₄ electrolyte.

FIG. 23 depicts nominal catalyst mass loadings for carbon inks dropcast on 5 mm RDEs. ^aMass loadings calculated for 10 μ L aliquots dropcast on glassy carbon RDEs based upon stock ink concentrations for each catalyst which were in the range of 1-1.5 mg mL^{-1} catalyst and 2.5-4.0 mg mL^{-1} Vulcan carbon powder. ^bElectroactive moles were calculated by integrating the Fe(III/II) redox wave visible in traces recorded under inert atmosphere in 0.1 M HClO_4 at a scan rate of 5 mV s^{-1} . ^c $(\text{phen}_2\text{N}_2)\text{FeCl}$ and $(\text{OEP})\text{FeCl}$ inks were prepared as 1.1 mg mL^{-1} catalyst mixtures in 2.5 mg mL^{-1} Vulcan carbon. ^d $(\text{Pc})\text{FeCl}$ inks were prepared as 1.5 mg mL^{-1} catalyst mixtures in 3.7 mg mL^{-1} Vulcan carbon. ^eFe-N-C catalyst ink was prepared without Vulcan carbon and had a concentration of 4.7 mg mL^{-1} . ^f $(\text{phen}_2\text{N}_2)\text{H}_2$ ink was prepared as a 0.9 mg mL^{-1} catalyst mixture in 2.7 mg mL^{-1} Vulcan carbon. ^gBare Vulcan carbon ink was prepared in a stock concentration of 10 mg mL^{-1} .

FIG. 24 depicts cyclic voltammograms of a rotating glassy carbon disk electrode modified with a catalyst film containing $(\text{phen}_2\text{N}_2)\text{FeCl}$ in N_2 - (black) and O_2 - (red) saturated 0.1 M HClO_4 aqueous electrolyte. Data were recorded at 5 mV s^{-1} and 2000 rpm rotation rate.

FIG. 25 depicts linear sweep voltammograms of various catalysts recorded in O_2 -saturated 0.1 M NaOH at a rotation rate of 2000 rpm and a scan rate of 5 mV s^{-1} (a) and Log(TOF) values derived from selected ORR polarization curves [shown in (a)] (b).

FIG. 26 depicts linear sweep voltammograms of glassy carbon disk electrodes modified with catalyst films containing Fe-N-C (black), $(\text{phen}_2\text{N}_2)\text{FeCl}$ (blue), $(\text{OEP})\text{FeCl}$ (orange), $(\text{Pc})\text{FeCl}$ (aqua), Vulcan carbon (green), and $(\text{phen}_2\text{N}_2)\text{H}_2$ (red) in O_2 -saturated 0.1 M HClO_4 electrolyte. Data were recorded at 5 mV s^{-1} and 2000 rpm rotation rate.

FIG. 27 depicts electrocatalytic ORR performance metrics and metal loadings for $(\text{phen}_2\text{N}_2)\text{FeCl}$, $(\text{OEP})\text{FeCl}$ and Fe-N-C. ^aV vs RHE. ^bDefined as the potential corresponding to an ORR current density of 0.1 mA cm^{-2} .

FIG. 28 depicts comparison of ORR linear sweep voltammogram traces for $(\text{phen}_2\text{N}_2)\text{FeCl}$ and $(\text{phen}_2\text{N}_2)\text{H}_2$ inks (a). Expansion of the onset region (b). The data were recorded at a rotation rate of 2000 rpm and a scan rate of 5 mV s^{-1} in 0.1 M NaOH.

FIG. 29 depicts Log(TOF) for ORR vs potential (a) for $(\text{phen}_2\text{N}_2)\text{FeCl}$ (blue), $(\text{OEP})\text{FeCl}$ (orange), and $(\text{Pc})\text{FeCl}$ (aqua). % H_2O_2 vs potential (b) for $(\text{phen}_2\text{N}_2)\text{FeCl}$ (blue), $(\text{OEP})\text{FeCl}$ (orange), $(\text{Pc})\text{FeCl}$ (aqua), and Fe-N-C (black). All data were recorded in saturated 0.1 M HClO_4 electrolyte at 5 mV s^{-1} and 2000 rpm rotation rate.

FIG. 30 depicts electroactive moles and turnover frequencies for (phen₂N₂)FeCl and (OEP)FeCl inks at select potentials.

FIG. 31 depicts RRDE plots of (phen₂N₂)FeCl (a), Fe-N-C (b), and (OEP)FeCl (c) in O₂-saturated 0.1 M HClO₄ aqueous electrolyte. All data were recorded at a rotation rate of 2000 rpm and 5 mV s⁻¹.

FIG. 32 depicts RRDE plots of (phen₂N₂)FeCl (a), Fe-N-C (b), and (OEP)FeCl (c) in O₂-saturated 0.1 M NaOH aqueous electrolyte. All data were recorded at a rotation rate of 2000 rpm and a scan rate of 5 mV s⁻¹.

FIG. 33 depicts %H₂O₂ produced during ORR catalysis as a function of potential in alkaline media. The traces are derived from RRDE data for (phen₂N₂)FeCl (blue), Fe-N-C (black) and (OEP)FeCl (orange) in 0.1 M NaOH aqueous electrolyte.

FIG. 34 depicts electrons transferred during ORR catalysis as a function of potential. The traces are derived from RRDE data for (phen₂N₂)FeCl (blue), Fe-N-C (black) and (OEP)FeCl (orange) in aqueous electrolyte, 0.1 M HClO₄ (a) and 0.1 M NaOH (b).

FIG. 35 depicts RRDE trace for (phen₂N₂)H₂ in 0.1 M NaOH. The inset shows an expansion of the ring current density (a). %H₂O₂ generated as a function of applied potential [derived from (a)] (b). Electrons transferred during ORR catalysis as a function of potential [derived from (a)] (c). Data were recorded at a rotation rate of 2000 rpm and a scan rate of 5 mV s⁻¹.

FIG. 36 depicts ORR linear sweep voltammogram traces for (phen₂N₂)FeCl (blue) and (phen₂N₂)H₂ (red) inks from Figure 6 with [(phen₂N₂)Fe]₂O (black) in 0.1 M HClO₄ (a) and 0.1 M NaOH (b). The data were recorded at 2000 rpm rotation rate and a scan rate of 5 mV s⁻¹.

FIG. 37 depicts XPS survey spectra of (phen₂N₂)H₂ (top), (phen₂N₂)Fe]₂O (middle) and [(OEP)Fe]₂O (bottom) powders mixed with Au powder and pressed onto carbon tape. Red labels refer to elements present in the molecular formula of the analyte while blue labels denote other elements.

FIG. 38 depicts XPS survey spectra of (phen₂N₂)FeCl (top), Fe-N-C (middle) and (OEP)FeCl (bottom) powders mixed with Au powder and pressed onto carbon tape. Red labels refer to elements present in the molecular formula of the analyte while blue labels denote other elements.

FIG. 39 depicts XPS high resolution N 1s spectra of $(\text{phen}_2\text{N}_2)\text{Fe}_2\text{O}$ (a), $(\text{phen}_2\text{N}_2)\text{FeCl}$ (b), $[(\text{OEP})\text{Fe}]_2\text{O}$ (c) and $(\text{OEP})\text{FeCl}$ (d) mixed with Au powder and pressed onto conductive carbon tape.

FIG. 40 depicts relative populations of iron environments in Fe-N-C derived from high-resolution XPS Fe 2p_{3/2} measurements.

FIG. 41 depicts XPS high resolution Fe 2p spectra of $(\text{phen}_2\text{N}_2)\text{Fe}_2\text{O}$ (top) and $(\text{phen}_2\text{N}_2)\text{FeCl}$ (bottom) mixed with Au powder and pressed onto conductive carbon tape.

FIG. 42 depicts XPS high resolution Fe 2p spectra of $[(\text{OEP})\text{Fe}]_2\text{O}$ (top) and $(\text{OEP})\text{FeCl}$ (bottom) mixed with Au powder and pressed onto conductive carbon tape.

FIG. 43 depicts comparison the pre-edge features from iron K-edge XANES spectra of $[(\text{phen}_2\text{N}_2)\text{Fe}]_2\text{O}$ (blue), Fe-N-C (black), $[(\text{OEP})\text{Fe}]_2\text{O}$ (orange) and $[(\text{Pc})\text{Fe}]_2\text{O}$ (aqua).

FIG. 44 depicts fits of EXAFS data for $[(\text{phen}_2\text{N}_2)\text{Fe}]_2\text{O}$ (a), $[(\text{OEP})\text{Fe}]_2\text{O}$ (b), and Fe-N-C (c). Real and imaginary components are shown as black and red traces respectively with fits given as dashed blue traces.

FIG. 45 depicts computed structure of $[(\text{phen}_2\text{N}_2)\text{Fe(III)}]^+$ visualized from the top and side.

FIG. 46 depicts linear sweep voltammograms of $(\text{phen}_2\text{N}_2)\text{FeCl}$ (blue), Vulcan carbon (green) and $\text{FeCl}_3/\text{Vulcan}$ (purple) inks polarized in O_2 -saturated 0.1 M HClO_4 electrolyte. All data were recorded at a rotation rate of 2000 rpm at a scan rate of 5 mV s⁻¹.

FIG. 47 depicts pH dependence of the Fe(III/II) redox couple of $(\text{phen}_2\text{N}_2)\text{FeCl}/\text{Nafion}/\text{Vulcan}$ ink in a modified aqueous Britton-Robinson buffer (50 mM each of NaHSO_4 , Na_2HPO_4 and B(OH)_3). pH values were adjusted by adding concentrated aqueous HClO_4 and/or NaOH .

FIG. 48 depicts zero-field Mössbauer spectrum of $[(\text{OEP})\text{Fe}]_2\text{O}$: ($\delta = 0.41 \text{ mm s}^{-1}$, $|\Delta E_Q| = 0.67 \text{ mm s}^{-1}$) recorded at 90 K.

FIG. 49 depicts zero-field Mössbauer spectrum of $[(\text{Pc})\text{Fe}]_2\text{O}$: ($\delta = 0.24 \text{ mm s}^{-1}$, $|\Delta E_Q| = 1.26 \text{ mm s}^{-1}$) recorded at 90 K.

DETAILED DESCRIPTION

Overview

The four-electron, four-proton reduction of molecular oxygen to water is the efficiency-limiting half reaction in low temperature fuel cells. Regardless of the fuel source used, the current density output is primarily limited by the slow electron transfer kinetics of the oxygen reduction reaction (ORR) taking place at the cathode. The sluggish kinetics involved in this half reaction necessitate high catalyst loadings at the cathode to generate practical current densities. The prototypical material for catalyzing this reaction in commercial fuel cells is platinum metal (Pt) supported on carbon. However, the high cost and scarcity of Pt impedes the large-scale deployment of fuel cell devices and motivates the development of Earth-abundant electrocatalysts for oxygen reduction. These catalysts must operate at low overpotentials and with high selectivity for the four-electron reduction of oxygen to water instead of the two-electron reduction process to generate hydrogen peroxide. Since early reports of oxygen reduction catalyzed by macrocyclic first-row transition metal complexes, there has been a global effort to develop selective and efficient ORR catalysts featuring base metal active sites.

Pyrolyzed iron- and nitrogen-doped (Fe-N-C) materials are leading Earth-abundant alternatives to Pt-based ORR electrocatalysts, however significant increases in catalyst performance are needed to make these materials technologically viable. Systematic improvement of these materials is hampered by the limited molecular-level understanding or control of the iron active sites. Fe-N-C materials are typically prepared by the high temperature pyrolysis of finely dispersed iron salts, porphyrins, or phthalocyanines along with a metal-organic framework (MOF) or carbon-based support. The uncontrolled nature of pyrolysis leads to a wide diversity of iron environments as well as extended solid iron phases in the resulting Fe-N-C materials. This poor control, combined with the wide variability in preparative procedures, has led to longstanding uncertainty about the local structure of the iron active sites responsible for ORR, thereby impeding systematic improvements to catalytic performance.

Numerous recent studies have provided significant insight into possible active site structures on Fe-N-C materials. While metallic iron has been postulated as an active site, mononuclear Fe-N₄ active sites are more commonly invoked to explain correlations between X-ray absorption spectroscopy (XAS) or ⁵⁷Fe Mössbauer spectroscopy with ORR activity. Despite the growing consensus that Fe-N₄ sites are essential for ORR, the ligation

environment of these iron sites remains uncertain. Indeed, even though iron porphyrin and phthalocyanine complexes can be used as precursors to Fe-N-C materials, there is growing appreciation that the core pyrrolic ligation environment of these precursors changes substantially upon pyrolysis. In particular, the first shell Fe-N bond lengths in Fe-N-C materials have been reported to be substantially shorter than the macrocyclic iron complex precursor used in the material synthesis. Furthermore, X-ray photoelectron spectroscopy (XPS) studies have pointed to the presence of metal-coordinated pyridinic nitrogen moieties as opposed to metal-bound pyrrolic nitrogens in Fe-N-C materials. ^{57}Fe Mössbauer spectra of many iron porphyrin and phthalocyanine complexes differ dramatically from main ^{57}Fe Mössbauer doublets assigned to the putative Fe-N₄ active sites in Fe-N-C materials. In addition, atomic-resolution TEM data indicate the presence of mono-dispersed iron atoms bound within the plane of graphitic carbon suggesting that the ligating groups are 6-membered heterocycles rather than the 5-membered rings found in porphyrins and phthalocyanines. Based on these spectroscopic and imaging results, there is a growing body of evidence that the Fe-N₄ sites in Fe-N-C materials are ligated by pyridinic moieties fused within graphitic.

Despite substantial evidence for *pyridinic* Fe-N₄ sites in Fe-N-C materials, nearly all molecular Fe-based ORR catalysts are macrocyclic complexes that feature *pyrrolic* coordination environments. Studies on homogeneous and adsorbed pyrrolic Fe complexes have shed significant insight into the mechanistic aspects of ORR including structure-function correlations and scaling relationships. However, the pyrrolic coordination environment of these molecular complexes makes them ineffective models for Fe-N-C materials, complicating spectroscopic assignments, and structure-activity correlations. Indeed, adsorbed pyrrolic Fe macrocycles generally display inferior activity and selectivity for ORR relative to Fe-N-C materials. Clearly, systematic progress in the understanding of Fe-N-C active sites and the rational design of improved catalysts requires new Fe-N₄ molecular complexes that can serve as high fidelity structural and functional mimics of Fe-N-C materials.

A better understanding of the catalytic active site can be developed via a bottom-up synthesis of molecular model complexes that mimic the spectroscopic features and catalytic ORR behavior of the pyrolyzed Fe-N-C catalyst. The D1 and D2 Mössbauer doublets believed to represent N₄Fe-sites are different from iron complexes of porphyrin

(refs. 19,20) and phthalocyanine, suggesting a structural change during pyrolysis and motivating the investigation. Refs. 21,22.

Examples of pyridinic N₄ macrocyclic ligands exist in the literature. Notably, the aza-bridged bis-1,10-phenanthroline hexaazamacrocyclic, (phen₂N₂)H₂ (phen₂N₂ = 1,14:7,8-diethenotetrapyrido[2,1,6-*de*:2',1',6'-*gh*:2'',1'',6''-*kl*:2''',1''',6'''-*na*][1,3,5,8,10,12]hexaazacyclotetradecine), as well as its cobalt(II), nickel(II) and copper(II) complexes have been reported and applied to DNA binding studies and carbon dioxide reduction catalysis. The present disclosure is related to the synthesis and characterization of this pyridinic Fe-N₄ macrocyclic fragment and compare its ⁵⁷Fe Mössbauer, XPS, and XAS features and ORR performance to those of prototypical Fe-N-C, iron octaethylporphyrin, (OEP)Fe, and iron phthalocyanine, (Pc)Fe, catalysts. It was demonstrated that the iron coordination environment in [(phen₂N₂)Fe]₂O closely resembles that of Fe-N-C materials and that (phen₂N₂)FeCl displays superior catalytic activity and selectivity relative to (OEP)FeCl and (Pc)FeCl, closely approaching the performance metrics of Fe-N-C materials. These studies establish (phen₂N₂)Fe complexes as high-fidelity structural and functional mimics of Fe-N₄ active sites in Fe-N-C materials.

A tetrapyridinic coordination complex bearing an extended π system capable of increased metal-ligand backbonding interactions should provide an accurate model of the pyrolyzed Fe-N-C catalyst. The resulting complex should be quite Lewis acidic, which has been shown to stabilize a dicationic metal, likely with some ligand-based radical character. Consequently, such a tetrapyridinic complex should be reduced at more anodic potentials relative to typical iron macrocycle complexes, thereby enabling superior ORR performance analogous to Fe-N-C materials.

Definitions

For convenience, before further description of the present invention, certain terms employed in the specification, examples and appended claims are collected here. These definitions should be read in light of the remainder of the disclosure and understood as by a person of skill in the art. Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by a person of ordinary skill in the art.

In order for the present invention to be more readily understood, certain terms and are defined below and throughout the specification.

The articles “a” and “an” are used herein to refer to one or to more than one (i.e., to at least one) of the grammatical object of the article. By way of example, “an element” means one element or more than one element.

The phrase “and/or,” as used herein in the specification and in the claims, should be understood to mean “either or both” of the elements so conjoined, i.e., elements that are conjunctively present in some cases and disjunctively present in other cases. Multiple elements listed with “and/or” should be construed in the same fashion, i.e., “one or more” of the elements so conjoined. Other elements may optionally be present other than the elements specifically identified by the “and/or” clause, whether related or unrelated to those elements specifically identified. Thus, as a non-limiting example, a reference to “A and/or B”, when used in conjunction with open-ended language such as “comprising” can refer, in one embodiment, to A only (optionally including elements other than B); in another embodiment, to B only (optionally including elements other than A); in yet another embodiment, to both A and B (optionally including other elements); etc.

As used herein in the specification and in the claims, “or” should be understood to have the same meaning as “and/or” as defined above. For example, when separating items in a list, “or” or “and/or” shall be interpreted as being inclusive, i.e., the inclusion of at least one, but also including more than one, of a number or list of elements, and, optionally, additional unlisted items. Only terms clearly indicated to the contrary, such as “only one of” or “exactly one of,” or, when used in the claims, “consisting of,” will refer to the inclusion of exactly one element of a number or list of elements. In general, the term “or” as used herein shall only be interpreted as indicating exclusive alternatives (i.e., “one or the other but not both”) when preceded by terms of exclusivity, such as “either,” “one of,” “only one of,” or “exactly one of.” “Consisting essentially of,” when used in the claims, shall have its ordinary meaning as used in the field of patent law.

As used herein in the specification and in the claims, the phrase “at least one,” in reference to a list of one or more elements, should be understood to mean at least one element selected from any one or more of the elements in the list of elements, but not necessarily including at least one of each and every element specifically listed within the list of elements and not excluding any combinations of elements in the list of elements. This definition also allows that elements may optionally be present other than the elements specifically identified within the list of elements to which the phrase “at least one” refers, whether related or unrelated to those elements specifically identified. Thus, as a non-

limiting example, “at least one of A and B” (or, equivalently, “at least one of A or B,” or, equivalently “at least one of A and/or B”) can refer, in one embodiment, to at least one, optionally including more than one, A, with no B present (and optionally including elements other than B); in another embodiment, to at least one, optionally including more than one, B, with no A present (and optionally including elements other than A); in yet another embodiment, to at least one, optionally including more than one, A, and at least one, optionally including more than one, B (and optionally including other elements); etc.

It should also be understood that, unless clearly indicated to the contrary, in any methods claimed herein that include more than one step or act, the order of the steps or acts of the method is not necessarily limited to the order in which the steps or acts of the method are recited.

In the claims, as well as in the specification above, all transitional phrases such as “comprising,” “including,” “carrying,” “having,” “containing,” “involving,” “holding,” “composed of,” and the like are to be understood to be open-ended, i.e., to mean including but not limited to. Only the transitional phrases “consisting of” and “consisting essentially of” shall be closed or semi-closed transitional phrases, respectively, as set forth in the United States Patent Office Manual of Patent Examining Procedures, Section 2111.03.

Structures depicted herein are also meant to include compounds that differ only in the presence of one or more isotopically enriched atoms. For example, compounds produced by the replacement of a hydrogen with deuterium or tritium, or of a carbon with a ^{13}C - or ^{14}C -enriched carbon are within the scope of this invention.

“Alkyl” refers to a fully saturated cyclic or acyclic, branched or unbranched carbon chain moiety having the number of carbon atoms specified, or up to 30 carbon atoms if no specification is made. For example, alkyl of 1 to 8 carbon atoms refers to moieties such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, and octyl, and those moieties which are positional isomers of these moieties. Alkyl of 10 to 30 carbon atoms includes decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl and tetracosyl. In certain embodiments, a straight chain or branched chain alkyl has 30 or fewer carbon atoms in its backbone (e.g., $\text{C}_1\text{-C}_{30}$ for straight chains, $\text{C}_3\text{-C}_{30}$ for branched chains), and more preferably 20 or fewer. Alkyl groups may be substituted or unsubstituted.

As used herein, the term “alkylene” refers to an alkyl group having the specified number of carbons, for example from 2 to 12 carbon atoms, that contains two points of

attachment to the rest of the compound on its longest carbon chain. Non-limiting examples of alkylene groups include methylene $-(CH_2)-$, ethylene $-(CH_2CH_2)-$, n-propylene $-(CH_2CH_2CH_2)-$, isopropylene $-(CH_2CH(CH_3))-$, and the like. Alkylene groups can be cyclic or acyclic, branched or unbranched carbon chain moiety, and may be optionally substituted with one or more substituents.

"Cycloalkyl" means mono- or bicyclic or bridged or spirocyclic, or polycyclic saturated carbocyclic rings, each having from 3 to 12 carbon atoms. Likewise, preferred cycloalkyls have from 3-10 carbon atoms in their ring structure, and more preferably have 3-6 carbons in the ring structure. Cycloalkyl groups may be substituted or unsubstituted.

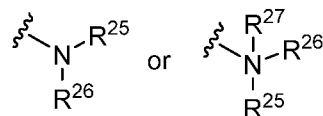
Unless the number of carbons is otherwise specified, "lower alkyl," as used herein, means an alkyl group, as defined above, but having from one to ten carbons, more preferably from one to six carbon atoms in its backbone structure such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, and tert-butyl. Likewise, "lower alkenyl" and "lower alkynyl" have similar chain lengths. Throughout the application, preferred alkyl groups are lower alkyls. In certain embodiments, a substituent designated herein as alkyl is a lower alkyl.

"Alkenyl" refers to any cyclic or acyclic, branched or unbranched unsaturated carbon chain moiety having the number of carbon atoms specified, or up to 26 carbon atoms if no limitation on the number of carbon atoms is specified; and having one or more double bonds in the moiety. Alkenyl of 6 to 26 carbon atoms is exemplified by hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl, octadecenyl, nonadecenyl, eicosenyl, heneicosoenyl, docosenyl, tricosenyl, and tetracosenyl, in their various isomeric forms, where the unsaturated bond(s) can be located anywhere in the moiety and can have either the (Z) or the (E) configuration about the double bond(s). Alkenyl groups may be substituted or unsubstituted.

"Alkynyl" refers to hydrocarbyl moieties of the scope of alkenyl, but having one or more triple bonds in the moiety.

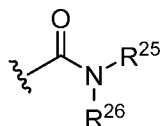
The terms "alkoxyl" or "alkoxy" as used herein refers to an alkyl group, as defined below, having an oxygen moiety attached thereto. Representative alkoxyl groups include methoxy, ethoxy, propoxy, tert-butoxy, and the like. An "ether" is two hydrocarbons covalently linked by an oxygen. Accordingly, the substituent of an alkyl that renders that alkyl an ether is or resembles an alkoxyl, such as can be represented by one of -O-alkyl, -O-alkenyl, or -O-alkynyl.

The terms “amine” and “amino” are art-recognized and refer to both unsubstituted and substituted amines, e.g., a moiety that can be represented by the formulae:



wherein R^{25} , R^{26} and R^{27} each independently represent a hydrogen, an alkyl, an alkenyl, an alkynyl, an aryl, a cycloalkyl, a cycloalkenyl, a heterocyclyl, or a polycyclyl.

The term “amide”, as used herein, refers to a group



wherein R^{25} and R^{26} are as defined above.

The term “aryl” as used herein includes 3- to 12-membered substituted or unsubstituted single-ring aromatic groups in which each atom of the ring is carbon (i.e., carbocyclic aryl) or where one or more atoms are heteroatoms (i.e., heteroaryl). Preferably, aryl groups include 5- to 12-membered rings, more preferably 6- to 10-membered rings. The term “aryl” also includes polycyclic ring systems having two or more cyclic rings in which two or more carbons are common to two adjoining rings wherein at least one of the rings is aromatic, e.g., the other cyclic rings can be cycloalkyls, cycloalkenyls, cycloalkynyls, aryls, heteroaryl, and/or heterocyclyls. Carbocyclic aryl groups include benzene, naphthalene, phenanthrene, phenol, aniline, and the like. Heteroaryl groups include substituted or unsubstituted aromatic 3- to 12-membered ring structures, more preferably 5- to 12-membered rings, more preferably 5- to 10-membered rings, whose ring structures include one to four heteroatoms. Heteroaryl groups include, for example, pyrrole, furan, thiophene, imidazole, oxazole, thiazole, triazole, pyrazole, pyridine, pyrazine, pyridazine and pyrimidine, and the like. Aryl and heteroaryl can be monocyclic, bicyclic, or polycyclic.

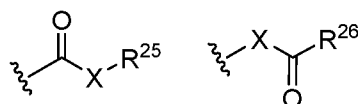
The term “halo”, “halide”, or “halogen” as used herein means halogen and includes, for example, and without being limited thereto, fluoro, chloro, bromo, iodo and the like, in both radioactive and non-radioactive forms. In one embodiment, halo is selected from the group consisting of fluoro, chloro and bromo.

The terms “heterocyclyl” or “heterocyclic group” refer to 3- to 12-membered ring structures, more preferably 5- to 12-membered rings, more preferably 5- to 10-membered rings, whose ring structures include one to four heteroatoms. Heterocycles can be monocyclic, bicyclic, spirocyclic, or polycyclic. Heterocyclyl groups include, for example,

thiophene, thianthrene, furan, pyran, isobenzofuran, chromene, xanthene, phenoxathiin, pyrrole, imidazole, pyrazole, isothiazole, isoxazole, pyridine, pyrazine, pyrimidine, pyridazine, indolizine, isoindole, indole, indazole, purine, quinolizine, isoquinoline, quinoline, phthalazine, naphthyridine, quinoxaline, quinazoline, cinnoline, pteridine, carbazole, carboline, phenanthridine, acridine, pyrimidine, phenanthroline, phenazine, phenarsazine, phenothiazine, furazan, phenoxazine, pyrrolidine, oxolane, thiolane, oxazole, piperidine, piperazine, morpholine, lactones, lactams such as azetidinones and pyrrolidinones, sultams, sultones, and the like. The heterocyclic ring can be substituted at one or more positions with such substituents as described above, as for example, halogen, alkyl, aralkyl, alkenyl, alkynyl, cycloalkyl, hydroxyl, amino, nitro, sulfhydryl, imino, amido, phosphate, phosphonate, phosphinate, carbonyl, carboxyl, silyl, sulfamoyl, sulfinyl, ether, alkylthio, sulfonyl, ketone, aldehyde, ester, a heterocyclyl, an aromatic or heteroaromatic moiety, $-\text{CF}_3$, $-\text{CN}$, and the like.

As used herein, the term “nitro” means $-\text{NO}_2$; the term “halogen” designates $-\text{F}$, $-\text{Cl}$, $-\text{Br}$, or $-\text{I}$; the term “sulfhydryl” means $-\text{SH}$; the term “hydroxyl” means $-\text{OH}$; the term “sulfonyl” means $-\text{SO}_2-$; the term “azido” means $-\text{N}_3$; the term “cyano” means $-\text{CN}$; the term “isocyanato” means $-\text{NCO}$; the term “thiocyanato” means $-\text{SCN}$; the term “isothiocyanato” means $-\text{NCS}$; and the term “cyanato” means $-\text{OCN}$.

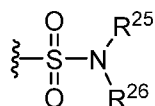
The term “carbonyl” is art-recognized and includes such moieties as can be represented by the general formula:



wherein X is a bond or represents an oxygen or a sulfur, and R^{25} and R^{26} are as defined above. Where X is an oxygen and R^{25} or R^{26} is not hydrogen, the formula represents an “ester”. Where X is an oxygen, and R^{25} is as defined above, the moiety is referred to herein as a carboxyl group, and particularly when R^{25} is a hydrogen, the formula represents a “carboxylic acid”. Where X is an oxygen, and R^{26} is hydrogen, the formula represents a “formate”. In general, where the oxygen atom of the above formula is replaced by sulfur, the formula represents a “thiocarbonyl” group. Where X is a sulfur and R^{25} or R^{26} is not hydrogen, the formula represents a “thioester” group. Where X is a sulfur and R^{25} is hydrogen, the formula represents a “thiocarboxylic acid” group. Where X is a sulfur and R^{26} is hydrogen, the formula represents a “thioformate” group. On the other hand,

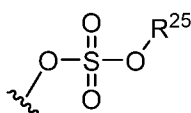
where X is a bond, and R²⁵ is not hydrogen, the above formula represents a “ketone” group. Where X is a bond, and R²⁵ is hydrogen, the above formula represents an “aldehyde” group.

The term “sulfonamide” is art-recognized and includes a moiety that can be represented by the formula:



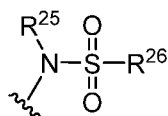
in which R²⁵ and R²⁶ are as defined above.

The term “sulfate” is art recognized and includes a moiety that can be represented by the formula:



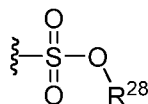
in which R²⁵ is as defined above.

The term “sulfonamide” is art recognized and includes a moiety that can be represented by the formula:



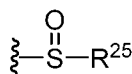
in which R²⁵ and R²⁶ are as defined above.

The term “sulfonate” is art-recognized and includes a moiety that can be represented by the formula:



in which R²⁸ is an electron pair, hydrogen, alkyl, cycloalkyl, or aryl.

The terms “sulfoxido” or “sulfinyl”, as used herein, refers to a moiety that can be represented by the formula:



in which R²⁵ is as defined above.

As used herein, the definition of each expression, e.g., alkyl, m, n, etc., when it occurs more than once in any structure, is intended to be independent of its definition elsewhere in the same structure.

The term “substituted” refers to moieties having substituents replacing a hydrogen or more carbons of the backbone. It will be understood that “substitution” or

“substituted with” includes the implicit proviso that such substitution is in accordance with permitted valence of the substituted atom and the substituent, and that the substitution results in a stable compound, e.g., which does not spontaneously undergo transformation such as by rearrangement, cyclization, elimination, etc. As used herein, the term “substituted” is contemplated to include all permissible substituents of organic compounds. In a broad aspect, the permissible substituents include acyclic and cyclic, branched and unbranched, carbocyclic and heterocyclic, aromatic and non-aromatic substituents of organic compounds. The permissible substituents can be one or more and the same or different for appropriate organic compounds. For purposes of this invention, the heteroatoms such as nitrogen may have hydrogen substituents and/or any permissible substituents of organic compounds described herein which satisfy the valences of the heteroatoms. Substituents can include any substituents described herein, for example, a halogen, a hydroxyl, a carbonyl (such as a carboxyl, an alkoxycarbonyl, a formyl, or an acyl), a thiocarbonyl (such as a thioester, a thioacetate, or a thioformate), an alkoxy, a phosphoryl, a phosphate, a phosphonate, a phosphinate, an amino, an amido, an amidine, an imine, a cyano, a nitro, an azido, a sulfhydryl, an alkylthio, a sulfate, a sulfonate, a sulfamoyl, a sulfonamido, a sulfonyl, a heterocyclyl, an aralkyl, or an aromatic or heteroaromatic moiety. In certain embodiments, the substituents on substituted alkyls are selected from C₁₋₆ alkyl, C₃₋₆ cycloalkyl, halogen, carbonyl, cyano, or hydroxyl. In other embodiments, the substituents on substituted alkyls are selected from fluoro, carbonyl, cyano, or hydroxyl. It will be understood by those skilled in the art that substituents can themselves be substituted, if appropriate. Unless specifically stated as “unsubstituted,” references to chemical moieties herein are understood to include substituted variants. For example, reference to an “aryl” group or moiety implicitly includes both substituted and unsubstituted variants.

For purposes of this invention, the chemical elements are identified in accordance with the Periodic Table of the Elements, CAS version, Handbook of Chemistry and Physics, 67th Ed., 1986-87, inside cover.

Compound Synthesis and Characterization

A prototypical Fe-N-C material was synthesized by a combination of literature methods. Briefly, Fe-N-C was prepared by pyrolysis of a mixture of iron(II) acetate, 1,10-phenanthroline and ZIF-8 metal organic framework under a reducing atmosphere (5% H₂ in

Ar). After pyrolysis, the sample was washed with 0.1 M H₂SO₄ to remove trace Fe(0). The ⁵⁷Fe Mössbauer spectrum of this material (FIG. 18, top) displays two quadrupole doublets. The narrow doublet, commonly referred to as the D1 doublet, displays an isomer shift (δ) of 0.46 mm s⁻¹ and a quadrupole splitting ($|\Delta E_Q|$) of 1.08 mm s⁻¹ and the wide doublet, commonly referred to as the D2 doublet, is characterized by $\delta = 0.37$ mm s⁻¹ and $|\Delta E_Q| = 3.06$ mm s⁻¹. These parameters are in line with previously reported Fe-N-C materials. These features were recently postulated to arise from Fe-N₄ sites existing in high-spin Fe(III) and low-spin Fe(II) states, respectively, although other assignments have been made previously, including D1 as a low spin Fe(II) site and D2 as an intermediate spin Fe(II) site.

The iron macrocyclic complex, (phen₂N₂)FeCl, can be obtained in five steps (FIG. 1). This scalable synthetic procedure has been optimized to furnish (phen₂N₂)FeCl in high yield, allowing large quantities of material to be produced, in contrast to many iron porphyrin complexes. (Phen₂N₂)FeCl and all synthetic intermediates are stable upon exposure to dioxygen and water and can be easily handled without special precautions.

The optical spectrum of (phen₂N₂)FeCl in MeCN (FIG. 2) is dominated by peaks centered at 223 and 266 nm in the UV region. These are $\pi \rightarrow \pi^*$ transitions with some metallic character. A series of low-intensity transitions in the low-UV and visible regions are due to lower-energy π -type transitions that have some Fe-Cl σ^* or π^* character. No absorptions are observed in the near IR region. Some reported tetraaza[14]annulene iron(III) chloride complexes give qualitatively similar spectra, albeit with a hypsochromic shift and increase in the complexity of the mid-spectrum peaks, presumably due to increased opportunities for ligand-based π^* transitions.

UV-Vis data of (phen₂N₂)FeCl in DMSO (FIG. 17) also support formation of the metalated complex with a bathochromic shift of the ligand $\pi \rightarrow \pi^*$ transitions and the appearance of shoulders on the main $\pi \rightarrow \pi^*$ peak. Additionally, the ligand peaks at 360 at 376 nm broaden and increase substantially in intensity relative to the main $\pi \rightarrow \pi^*$ peak upon metalation. A new peak appears at 429 nm, while the broad, low-intensity ligand peaks at 439 and 467 nm vanish. The resulting spectrum upon metalation is similar to spectra of tetraaza[14]annulene iron(III) chloride complexes in DMSO.

The ⁵⁷Fe Mössbauer spectrum of (phen₂N₂)FeCl (FIG. 18, middle) reveals a major quadrupole doublet assigned to (phen₂N₂)FeCl and a minor doublet assigned to residual Fe₂Cl₆·(DMF)₃. The major quadrupole doublet for (phen₂N₂)FeCl is described by $\delta = 0.39$ mm s⁻¹ and $|\Delta E_Q| = 3.06$ mm s⁻¹. These parameters are dramatically different from those of

(OEP)FeCl which displays an δ of 0.30 mm s⁻¹ and a $|\Delta E_Q|$ of 0.60 mm s⁻¹. Additionally, they also differ from those of (Pc)FeCl which is characterized by an δ of 0.28 mm s⁻¹ and a $|\Delta E_Q|$ of 2.95 mm s⁻¹. The particularly large $|\Delta E_Q|$ observed for (phen₂N₂)FeCl suggests that the iron center exists in an $S = 3/2$ intermediate spin state or an $S = 3/2$, $5/2$ admixture spin state as has been observed for other iron(III) N₄ macrocycles complexes. This assignment is consistent with our calculations on (phen₂N₂)FeCl, which predict an intermediate-spin ground state. This electronic structure is consistent with a compressed N₄-binding pocket (see below) that stabilizes the $S = 3/2$ spin state. Although the ⁵⁷Fe Mössbauer parameters for (phen₂N₂)FeCl are similar to those of the D2 doublet in Fe-N-C, we caution against overinterpreting this similarity because ⁵⁷Fe Mössbauer spectra are highly sensitive to axial ligation (see below) and the axial Cl in (phen₂N₂)FeCl is distinct from the putative OH_x ligand present in Fe-N-C materials.

To better mimic the axial O-ligation present in the material, (phen₂N₂)FeCl was subjected to Soxhlet extraction with ethanol. This served to remove some residual iron salts and generate the μ -oxo [(phen₂N₂)Fe]₂O via reaction with adventitious water and base. Similar conversions are well-documented for sterically unprotected porphyrin complexes. While this species is catalytically inactive in acidic electrolyte, it provides a good spectroscopic model for Fe-N-C materials and the analogous [(OEP)Fe]₂O, and [(Pc)Fe]₂O were synthesized by literature methods for comparison.

The ⁵⁷Fe Mössbauer spectrum of the [(phen₂N₂)Fe]₂O complex is a doublet (FIG. 18, bottom), described by $\delta = 0.45$ mm s⁻¹ and $|\Delta E_Q| = 0.87$ mm s⁻¹. Our sample of [(OEP)Fe]₂O displays ⁵⁷Fe Mössbauer parameters of $\delta = 0.41$ mm s⁻¹ and $|\Delta E_Q| = 0.67$ mm s⁻¹. Likewise, our sample of [(Pc)Fe]₂O displays ⁵⁷Fe Mössbauer parameters of $\delta = 0.25$ mm s⁻¹ and $|\Delta E_Q| = 1.26$ mm s⁻¹. Notably, the ⁵⁷Fe Mössbauer parameters for both [(OEP)Fe]₂O, and [(phen₂N₂)Fe]₂O as well as other μ -oxo compounds are within the range of values reported for the D1 doublet in Fe-N-C materials. The δ and $|\Delta E_Q|$ values which characterize [(Pc)Fe]₂O are outside the typical values for the D1 doublet, however some reported values for Fe-N-C derived from pyrolyzed iron porphyrins are close. The vast differences in the ⁵⁷Fe Mössbauer spectra of (phen₂N₂)Fe, (OEP)Fe, and (Pc)Fe upon exchange of the axial ligand suggest that ⁵⁷Fe Mössbauer spectroscopy alone may be insufficient to distinguish pyrrolic from pyridinic ligation at putative Fe-N₄ sites in Fe-N-C materials.

The near-edge feature in the X-ray absorption spectrum (XAS) of (phen₂N₂)FeCl is consistent with a symmetric complex bearing a two-fold rotational axis and is similar in position to OEPFeCl. The pre-edge feature located at 7114.3 eV is quantitatively similar to that given by a pyrolyzed Fe-N-C sample synthesized by a combination of published methods^{8,25} with slight alterations (FIG. 3). Structural parameters derived from the k²-weighted Fourier transform of the iron k-edge EXAFS data (FIG. 4) as well as the similar shape of the XANES spectrum for both (phen₂N₂)FeCl and Fe-N-C indicate analogous coordination environments (Table 1).

Table 1. Iron k-edge Fourier transform fitting parameters.

Sample	Scattering Path	CN	R (Å)	$\Delta\sigma^2$ (Å ²)	ΔE_0 (eV)	Pre-edge energy (keV)	XANES energy (keV)
(phen ₂ N ₂)FeCl	Fe-N	4.3	1.93	0.005	-1.5	7.1143	7.1223
	Fe-Cl	1.0	2.33	0.004			
	Fe-O	0.7	1.99	0.001			
(phen ₂ N ₂)Fe	Fe-N	4.0	1.94	0.005	-1.0	7.1137	7.1222
	Fe-Cl	0.7	2.35	0.004			
Fe-N-C	Fe-N	4.0	1.94	0.005	-5.5	7.1142	7.1257
	Fe-O	1.7	2.04	0.001			
Fe-N-C (reduced)	Fe-N	4.0	1.99	0.005	-4.5	7.1142	7.1240

These results strongly suggest a structural resemblance between the iron atoms in Fe-N-C and (phen₂N₂)FeCl with Fe-N vectors of 1.94 and 1.93 Å, respectively.

The nitrogen environments present in Fe-N-C, [(phen₂N₂)Fe]₂O, (phen₂N₂)H₂, [(OEP)Fe]₂O, and [(Pc)Fe]₂O were analyzed by X-ray photoelectron spectroscopy (XPS). For Fe-N-C, we observed a broad N 1s XPS signal similar to that reported for other Fe-N-C materials (FIG. 19, a). The N peak envelope for Fe-N-C spans from 396 to 407 eV and can be deconvoluted into four peaks, previously assigned to oxidized (404.0 eV), graphitic/pyrrolic (401.3 eV), metal-coordinated (399.9 eV) and pyridinic nitrogen (398.3 eV). This sample was prepared by pyrolysis of a zinc imidazolate MOF, ZIF-8, therefore

the metal-coordinated N peak is expected to result from both iron and zinc coordination. Literature reports suggest that the binding energy of the coordinated N peak is largely insensitive to metal identity.

The very broad peak envelope for Fe-N-C contrasts with the well-defined nitrogen environments in [(OEP)Fe]₂O, [(Pc)Fe]₂O, and [(phen₂N₂)Fe]₂O. For [(phen₂N₂)Fe]₂O, high resolution N 1s spectra (FIG. 19, b) reveal a single broad peak centered at 399.3 eV that can be deconvoluted into two components centered at 398.3 and 399.6 eV with a peak integration ratio of 1:2. Based on the integration ratio and the symmetry of the (phen₂N₂)Fe subunits in [(phen₂N₂)Fe]₂O, we assign the 398.3 peak to the bridgehead nitrogen atoms and the 399.6 peak to the coordinated pyridine nitrogen atoms. In comparison, the N 1s XPS spectrum (FIG. 20, bottom) of (phen₂N₂)H₂ is dominated by two peaks corresponding to bridging and pyridinic nitrogen atoms at 397.9 and 399.4 eV, respectively in a 1:2 ratio. This indicates that both bridging and pyridinic nitrogen atoms shift to higher binding energies upon metalation with iron. Similar changes in the N 1s spectrum have been reported for free-base porphyrins upon metalation. In contrast, the XPS N 1s spectra of [(OEP)Fe]₂O and [(Pc)Fe]₂O differ markedly from that of [(phen₂N₂)Fe]₂O. The spectrum of [(OEP)Fe]₂O consists of a sharp peak at 397.6 eV with a broad satellite peak centered at 400.0 eV (FIG. 19, c). The spectrum of [(Pc)Fe]₂O is similar with a sharp peak at 398.4 eV with a satellite peak centered at 400.1 eV (FIG. 19, d). N 1s peaks for (phen₂N₂)FeCl, (OEP)FeCl, (Pc)FeCl appear within 0.3–0.4 eV of the corresponding peaks for the μ -oxo compounds, indicating that the identity of the axial ligand does not impact the N 1s binding energy to the same extent as does changing the nature of the metal-coordinated nitrogen atoms from pyrrolic to pyridinic. Importantly, the N 1s peaks for the coordinated pyridinic nitrogen atoms in the (phen₂N₂)Fe complexes match well with the peak corresponding to the metal-coordinated pyridinic nitrogen component (399.9 eV) of Fe-N-C, whereas the N 1s peaks of the coordinated pyrrolic nitrogen atoms in (OEP)Fe and (Pc)Fe complexes appear at significantly lower binding energies. Together, the XPS data indicate that the iron-coordinated N environment in [(phen₂N₂)Fe] species are electronically very similar to the metal-coordinated N environments in Fe-N-C materials.

The iron environments present in Fe-N-C, [(phen₂N₂)Fe]₂O, [(OEP)Fe]₂O, and [(Pc)Fe]₂O were also examined by XPS. Consistent with previously reported data of Fe-N-C materials, we observe Fe 2p_{3/2} peaks at 709.8 and 713.5 eV (FIG. 19, e) assigned to Fe(II) and Fe(III) formal oxidation states, respectively. In contrast, [(OEP)Fe]₂O (FIG. 19, g)

displays Fe 2p_{3/2} and 2p_{1/2} peaks at 709.3 and 723.3 eV, respectively. Similarly, [(Pc)Fe]₂O (FIG. 19, h) exhibits Fe 2p_{3/2} and 2p_{1/2} peaks at 708.9 and 722.0 eV, respectively.

Significant asymmetry on the main Fe 2p_{3/2} peak for both [(OEP)Fe]₂O and [(Pc)Fe]₂O compounds was observed. The asymmetry is attributed to multiplet splitting and is thought to arise from core-hole interactions with the open-shell electronic structure of the high-spin ferric centers. Similar features are observed for (OEP)FeCl and (Pc)FeCl, albeit with a ~0.7–0.9 eV shift to higher binding energy. These XPS features are distinct from those observed for [(phen₂N₂)Fe]₂O (FIG. 19, f) which displays Fe 2p_{3/2} and 2p_{1/2} peaks at 710.8 and 724.3 eV. We note that (phen₂N₂)FeCl shows Fe 2p_{3/2} and 2p_{1/2} peaks at similar binding energies, 710.8 and 724.7 eV, respectively, and that residual FeCl₃ salts are likely to be subsumed into these peaks. As with [(OEP)Fe]₂O and [(Pc)Fe]₂O, we also observe significant asymmetry in the Fe 2p_{3/2} peak of [(phen₂N₂)Fe]₂O that we also attribute to core-hole interactions with an open-shell ferric center. There is also some asymmetry to the Fe 2p_{1/2} peak which likely originates from the same effect. Importantly, we observe a >1.5 eV shift to higher binding energy for the main Fe 2p_{3/2} peak for [(phen₂N₂)Fe]₂O relative to both [(OEP)Fe]₂O and [(Pc)Fe]₂O. This observation is consistent with increased π -acidity of the pyridinic macrocycle in [(phen₂N₂)Fe]₂O, which withdraws electron density from the iron center. Notably, the peak in Fe-N-C previously assigned to Fe(III) is 2.7 eV positive of the corresponding Fe(III) peak for [(phen₂N₂)Fe]₂O but even more positive than the same peak in [(OEP)Fe]₂O and [(Pc)Fe]₂O. These data suggest that while the Fe(III) centers in Fe-N-C may exist in an even more withdrawing ligation environment, a pyridinic macrocycle complex such as [(phen₂N₂)Fe]₂O provides a better structural model for Fe-N-C than pyrrolic macrocycles such as [(OEP)Fe]₂O and [(Pc)Fe]₂O. Indeed, the strongly electron withdrawing environment in the material helps to explain the positive shift of the putative Fe(II) component of Fe-N-C, which makes it appear close in energy to the main Fe 2p_{3/2} peaks for both of the Fe(III) complexes examined here. Taken as a whole, the XPS data are consistent with nitrogen and iron environments in [(phen₂N₂)Fe]₂O that are more electropositive than a typical pyrrolic macrocycle and more similar to the metal-N_x sites in Fe-N-C.

XPS results (FIG 5.) for (phen₂N₂)FeCl are consistent with a complex with a N:Cl:Fe ratio of 6:1:1 (Table 2) and indicate substantial electronic changes as a result of metal coordination to the dianionic species, (phen₂N₂)²⁻.

XAS results demonstrate a strong resemblance between Fe-N-C and $[(\text{phen}_2\text{N}_2)\text{Fe}]_2\text{O}$. We next examined the electronic structure and coordination environment of the iron centers in Fe-N-C, $[(\text{phen}_2\text{N}_2)\text{Fe}]_2\text{O}$, $[(\text{OEP})\text{Fe}]_2\text{O}$, and $[(\text{Pc})\text{Fe}]_2\text{O}$ by X-ray absorption spectroscopy (XAS). The XANES spectrum of our Fe-N-C preparation (FIG. 21, a, black) matches those reported in the literature. While a rigorous analysis of the X-ray absorption near edge structure (XANES) spectra for Fe-N-C materials is challenging due to the presumed presence of a mixture of Fe(II) and Fe(III) as well as an unknown degree of heterogeneity in the local coordination environment of each iron, the XANES line shapes have been exhaustively examined for a wide variety of pyrolyzed Fe-N-C catalysts and features of the XANES have been correlated to ORR activity. In particular, the intensity of the first main edge peak, C, has been found to positively correlate with ORR activity, whereas the intensities of the main edge shoulder, B, and the higher energy main edge peak, D, have been shown to anticorrelate with ORR activity (FIG. 21, a, dotted vertical lines). Notably, the XANES spectra of $[(\text{OEP})\text{Fe}]_2\text{O}$ (FIG.21, a, orange) and $[(\text{Pc})\text{Fe}]_2\text{O}$ shows enhanced intensity for D with $[(\text{OEP})\text{Fe}]_2\text{O}$ also showing enhanced intensity for B. These features contrast the XANES spectra of $[(\text{phen}_2\text{N}_2)\text{Fe}]_2\text{O}$ (FIG.21, a, blue), which shows a higher intensity for C, and lower intensities for B and D. The intensity of pre-edge peak, A, has also been shown to positively correlate with ORR activity. We find that the pre-edge peak line shape for $[(\text{phen}_2\text{N}_2)\text{Fe}]_2\text{O}$ matches closely with that of Fe-N-C, but that the peak intensity for both is lower than that for $[(\text{OEP})\text{Fe}]_2\text{O}$ and dramatically lower than the sharp pre-edge feature observed for $[(\text{Pc})\text{Fe}]_2\text{O}$. Given the high sensitivity of the pre-edge peak to the identity of the axial ligand in similar tetrapyrrolic complexes as well as distortions in the Fe-N₄ plane made possible by variation of the Fe-O-Fe angle in $[(\text{OEP})\text{Fe}]_2\text{O}$ and $[(\text{Pc})\text{Fe}]_2\text{O}$, we refrain from overinterpreting the pre-edge peak shapes or intensity. Nonetheless, the suppressed intensity at B and D and increased intensity at C for $[(\text{phen}_2\text{N}_2)\text{Fe}]_2\text{O}$ suggests that the $(\text{phen}_2\text{N}_2)\text{Fe}$ molecular analogue is a superior model for the active sites in Fe-N-C materials relative to pyrrolic macrocycles.

Extended X-ray absorption fine structure (EXAFS) data provide further evidence in support of the structural similarity between the iron coordination environments in $[(\text{phen}_2\text{N}_2)\text{Fe}]_2\text{O}$ and Fe-N-C. The k^2 -weighted EXAFS oscillations for Fe-N-C (FIG. 21, b, black) exhibit remarkably similar amplitudes and periods to the EXAFS of $[(\text{phen}_2\text{N}_2)\text{Fe}]_2\text{O}$ (FIG.21, b, blue) out to $\sim 10.0 \text{ \AA}^{-1}$ with only a small phase shift beyond $\sim 6.0 \text{ \AA}^{-1}$. In contrast, the k^2 -weighted EXAFS for $[(\text{OEP})\text{Fe}]_2\text{O}$ (FIG.21, b, orange) and $[(\text{Pc})\text{Fe}]_2\text{O}$

(FIG.21, b, aqua) displays amplitudes and periods that differ dramatically from the EXAFS of $[(\text{phen}_2\text{N}_2)\text{Fe}]_2\text{O}$ and Fe-N-C beyond $\sim 3.5 \text{ \AA}^{-1}$.

The similarity between Fe-N-C and $[(\text{phen}_2\text{N}_2)\text{Fe}]_2\text{O}$ is also reflected in the k^2 -weighted Fourier transform EXAFS radial distribution spectra (FIG.21, c). The $[(\text{phen}_2\text{N}_2)\text{Fe}]_2\text{O}$ complex displays a broad primary coordination shell scattering peak at $1.36 \text{ \AA}$ apparent distance, similar to the first shell peak for Fe-N-C at $1.46 \text{ \AA}$ apparent distance. In contrast, the first shell scattering peak for $[(\text{OEP})\text{Fe}]_2\text{O}$ and $[(\text{Pc})\text{Fe}]_2\text{O}$ appears at $1.62 \text{ \AA}$ and $1.47 \text{ \AA}$ apparent distance and display prominent shoulders at lower apparent distances that are not observed in Fe-N-C or $[(\text{phen}_2\text{N}_2)\text{Fe}]_2\text{O}$. Likewise, both $[(\text{phen}_2\text{N}_2)\text{Fe}]_2\text{O}$ and Fe-N-C have no prominent scattering interactions beyond $2 \text{ \AA}$, whereas significant higher order scattering is observed for $[(\text{OEP})\text{Fe}]_2\text{O}$, and $[(\text{Pc})\text{Fe}]_2\text{O}$. Taking together, the raw EXAFS data for Fe-N-C mostly matches by the spectrum of $[(\text{phen}_2\text{N}_2)\text{Fe}]_2\text{O}$ and is quite distinct from that of either $[(\text{OEP})\text{Fe}]_2\text{O}$ or $[(\text{Pc})\text{Fe}]_2\text{O}$.

The EXAFS peaks for all four materials are well modeled with a five-coordinate Fe center bearing four equatorial Fe-N scatterers and one axial Fe-O scatterer. The fits from modeling the data return Fe-N scattering paths of 1.94 , 1.97 , 2.06 , and $1.94 \text{ \AA}$ for Fe-N-C, $[(\text{phen}_2\text{N}_2)\text{Fe}]_2\text{O}$, $[(\text{OEP})\text{Fe}]_2\text{O}$, and $[(\text{Pc})\text{Fe}]_2\text{O}$, respectively. The Fe-N distances for both $[(\text{OEP})\text{Fe}]_2\text{O}$ and $[(\text{Pc})\text{Fe}]_2\text{O}$ agree with the corresponding distances extracted from crystal structures. Importantly, these Fe-N bond lengths reflect not only the N-N separation in the ligand, but also the degree of pucker of the Fe center out of the equatorial plane. Thus, this distance alone cannot distinguish pyridinic from pyrrolic ligation and, indeed, we see similar Fe-N vectors for $[(\text{phen}_2\text{N}_2)\text{Fe}]_2\text{O}$ and $[(\text{Pc})\text{Fe}]_2\text{O}$. Furthermore, for $[(\text{phen}_2\text{N}_2)\text{Fe}]_2\text{O}$, the $1.97 \text{ \AA}$ Fe-N distance extracted from EXAFS modeling is substantially higher than the $1.86 \text{ \AA}$ distance predicted from calculation if the Fe were to reside in the N_4 plane for the phen_2N_2 ligand, further evincing that the Fe center is puckered. This reasoning is also in line with a computational XAS study that showed an enhancement of the main edge peak C (FIG.21, a, blue) as the displacement of Fe from the N_4 plane was increased.³³ Consistent with the Fe-N-C material having a putative OH_x axial ligand, the EXAFS fits return an Fe-O scattering path of $2.04 \text{ \AA}$, slightly larger than the range of Fe-O scattering paths, 1.79 - $1.73 \text{ \AA}$, extracted for the molecular μ -oxo complexes. Taking both the raw k^2 -weighted EXAFS oscillations and the Fourier transform EXAFS spectra into account, the XAS data highlight that $[(\text{phen}_2\text{N}_2)\text{Fe}]_2\text{O}$ is a particularly good model of the Fe sites in Fe-N-C catalysts.

Table 2. C-, N-, O-, Fe- and Cl-content for (phen₂N₂)FeCl and Fe-N-C derived from XPS measurements.

Sample	at% C	at% N	at% O	at% Fe	at% Cl
(phen ₂ N ₂)FeCl	64.80	9.45	10.66	1.28	1.87
Fe-N-C	85.07	5.58	8.42	0.13	-

N 1s and N 2p XPS data for (phen₂N₂)H₂, and its cobalt, nickel and copper complexes have been reported.²⁶ In comparison, the N 1s peak of (phen₂N₂)FeCl is shifted to higher binding energy (399.7 eV) and can be modeled as two components centered at 399.1 and 399.9 eV with an area ratio of 1:2 (FIG. 5, A). The two peaks reported for (phen₂N₂)H₂ coalesce as the four pyridinic nitrogen atoms move following iron coordination. Similar alterations in the N 1s spectrum have been reported for different free-base porphyrins upon metallation.²⁷ The iron environment of (phen₂N₂)FeCl (FIG. 5, B) is consistent with other Fe(III) macrocyclic complexes²⁸ and characterized by Fe 2p_{1/2} and Fe 2p_{3/2} peaks located at 724.1 and 710.6 eV, respectively.

By comparison, Fe-N-C shows a broadened N1s peak which can be deconvoluted into four peaks, consistent with oxidized (405.5 eV), graphitic/pyrrolic (400.8 eV), Fe-N (399.1 eV) and pyridinic nitrogen (398.3 eV) (FIG. 5, A, top; Table 3).²⁹

Table 3. Relative populations of nitrogen environments in Fe-N-C derived from high-resolution XPS N 1s measurements.

	% Pyridinic N	% M-N	% Pyrrolic/Graphitic N	% Oxidized N
Fe-N-C	42.01	33.19	13.44	11.34

Overlap with the (phen₂N₂)FeCl N 1s peak is consistent with the metal-coordinated pyridinic nitrogen component (399.1 eV) evident upon deconvolution. There is overlap between Fe 2p_{3/2} peaks for (phen₂N₂)FeCl and Fe-N-C, but a notable shift is evident between the position of the iron(III) component in each sample. This is attributed to the highly Lewis acidic environment surrounding in-plane surface-confined iron atoms (FIG. 5,

B). Little Fe(0) is observed, consistent with the FT-EXAFS data, and a mixture of Fe(III) and Fe(II) is clearly indicated (Table 4), consistent with the XANES results.

Table 4. Relative populations of iron environments in Fe-N-C derived from high-resolution XPS Fe 2p measurements.

	% Fe(II)	% Fe(III)
Fe-N-C	35.40	64.60

The ratio of Fe to Fe-N-type nitrogen in the Fe-N-C catalyst is close to 1:4, as expected.

(Phen₂N₂)FeCl is best described as an S=3/2 spin system, in good agreement with computational results. The zero-field Mössbauer spectrum of (phen₂N₂)FeCl presents as a quadrupole doublet ($\delta = 0.39 \text{ mm s}^{-1}$ and $|\Delta E_Q| = 3.06 \text{ mm s}^{-1}$, FIG. 6, A) most consistent with an intermediate spin system and similar in magnitude to previously reported porphyrin,^{19,30-34} porphycene,³⁵ tetraazaannulene²⁴ iron(III) complexes bearing various substitutions (Table 5).

Table 5. Zero-Field Mössbauer Parameters of (phen₂N₂)FeCl, (phen₂N₂)Fe, Fe-N-C and D1/D2 Doublets Present in Reported Pyrolyzed Fe/N/C Materials.

Complex or material (preparative method)	Spectral Component	Structural Assignment	$\delta,^a \text{ mm s}^{-1}$	$ \Delta E_Q , \text{ mm s}^{-1}$	T, K	Active Site for ORR	Reference
(phen ₂ N ₂)Fe ^{III} Cl	-		0.39	3.06	90	-	This work
(phen ₂ N ₂)Fe ^{II}	-		0.44	0.93	90	FeN ₄	This work
Fe-N-C (pyrolyzed ZIF-8 MOF)	D1	Fe ^{II} N ₄ , LS	0.49	1.17	90	FeN _x	This work
	D2						
Fe/N/C (pyrolyzed ZIF-8 MOF) ¹⁸	D1	Fe ^{II} N ₄ , LS	0.36	0.98	293		<i>Nat. Mater.</i> 2015 , <i>14</i> , 937–942.
	D2		0.40	2.59			
Phen/PANI Additive Fe/N/C ²⁰			0.30	0.86	70		<i>J. Am. Chem. Soc.</i> 2014 , <i>136</i> , 978–985.

T(<i>p</i> -OCH ₃) PPFe ²¹	D1	Fe ^{II} N ₄ , LS	0.41	0.61	77	-	J. Chem. Soc. Faraday Trans. 1 1981 , 77, 2827–2843.
TPPFeCl (pyrolyzed) ²²	D1	Fe ^{II} N ₄ , LS	0.63	0.96	130		Angew. Chem. Int. Ed. 1999 , 38, 3181–3183.
Fe/N/C (ZIF-8 MOF) ²³	D1	Fe ^{II} N ₄ , LS	0.37	0.74	298		J. Phys. Chem. Lett. 2014 , 5, 3750–3756.
	D2	Fe ^{II} N ₄ , IS	0.32	2.63			
	D3	Fe ^{II} N ₄ , HS	1.00	2.21			
	Sextet	Iron Carbide	0.13	0.08			

A previously reported $S = 3/2$ iron(III) iodide complex of a dianionic N₄ macrocyclic ligand³⁶ shows similar Mössbauer parameters ($\delta = 0.18 \text{ mm s}^{-1}$ and $|\Delta E_Q| = 3.56 \text{ mm s}^{-1}$)³⁷ although the relatively elevated isomer shift and smaller quadrupole splitting values of (phen₂N₂)FeCl may indicate a slight $S = 3/2$, $5/2$ admixture. The Mössbauer parameters of various $S=3/2$ iron(III) porphyrins are more similar to (phen₂N₂)FeCl.³⁸⁻⁴⁰

Chemical reduction of (phen₂N₂)FeCl with Cp₂Co under inert atmosphere results in a reduction in the intensity of the Fe-Cl bond vector as well as a shift to lower pre-edge and XANES energies (FIG. 3 and Table 1). Analogous reduction of Fe-N-C displays an increase in the intensity of the pre-edge feature along with a decrease in the intensity evident in the FT-EXAFS data, indicating removal of axially-bound ligands from the iron-containing sites in the material. The zero-field Mössbauer spectrum of reduced (phen₂N₂)FeCl (FIG. 6, B) is represented by a single quadrupolar doublet with $\delta = 0.44 \text{ mm s}^{-1}$ and $|\Delta E_Q| = 0.93 \text{ mm s}^{-1}$. These values indicate a correspondence to the D1 doublet reported for a range of synthetic Fe-N-C preparations (Table 5) with median δ and $|\Delta E_Q|$ values of 0.45 mm s^{-1} and 0.89 mm s^{-1} , respectively.

Electrochemical Studies

Homogeneous:

The initial electrochemical characterization of (phen₂N₂)FeCl was performed under inert atmosphere in *N,N'*-dimethylformamide containing a slight molar excess of Tl(OTf) and 60 mM [DMF-H][OTf] (FIG. 15). The Fe(III/II) couple is found to be located at -0.158 V vs Cp₂Fe⁺/Cp₂Fe which is several hundred millivolts more positive of most reported iron porphyrins in similar solvent and electrolyte mixtures.⁴¹

Heterogeneous:

Samples of (phen₂N₂)FeCl and pyrolyzed Fe-N-C were independently processed into heterogeneous inks and dropcast onto polished glassy carbon rotating disk electrodes. Cyclic voltammograms taken in 0.1 M HClO₄ under Ar-atmosphere (FIG. 7) demonstrate that (phen₂N₂)FeCl and Fe-N-C have similar redox potentials, far anodic of that displayed by a comparable porphyrin such as OEPFeCl (0.27 V vs RHE). These reversible waves are assigned as the Fe(III/II) redox couple for each catalyst. Introduction of an O₂-atmosphere in the presence of (phen₂N₂)FeCl gives a catalytic wave whose $E_{1/2}$ potential roughly corresponds to the reversible wave observed under inert atmosphere (FIG. 8), both confirming that (phen₂N₂)FeCl is a ORR catalyst and validating the assignment of the redox couple. In both acidic and basic media (phen₂N₂)FeCl displays improved ORR onset values (0.74 V and 0.88 V vs RHE, respectively) compared to OEPFeCl (0.45 V and 0.74 V vs RHE, respectively). This suggests a substantial difference in ORR performance based upon the primary coordination sphere and correlates with the shift in the $E_{1/2}$ value.

The relative electrochemical ORR activities and behavior of both (phen₂N₂)FeCl and Fe-N-C were then examined. In comparison to the Fe-N-C materials, (phen₂N₂)FeCl displays inferior activity (FIG. 9, blue and black traces) and stability in acidic conditions (FIG. 11). In basic media, the stability and activity of (phen₂N₂)FeCl are improved, with more positive onset potentials, slower degradation (see FIG. 12, (a) and (b)) and a closer match to the performance of Fe-N-C materials (see Table 6).

(Phen₂N₂)Fe displays an Fe(III/II) redox potential higher than (OEP)Fe and more similar to Fe-N-C. Both model compounds and the Fe-N-C material were evaluated electrochemically as thin films supported on glassy carbon electrodes. In a typical preparation, Fe-N-C powders were dispersed in a 7:2:1 combination of CH₂Cl₂, ethanol, and 5 wt% Nafion solution (75 wt% ethanol and 20 wt% water), respectively. The resulting inks were dropcast onto a glassy carbon disk electrode and allowed to dry in air to generate a well-adhered catalyst film. A similar procedure was used for (phen₂N₂)FeCl and (OEP)FeCl with inclusion of Vulcan carbon powder to enhance film conductivity. We expect that any residual FeCl₃ salts present in the (phen₂N₂)FeCl sample will readily dissolve into the acidic electrolyte and will, therefore, not impact the electrochemical results. In line with this expectation, we find that FeCl₃/Vulcan inks are inactive for ORR.

Cyclic voltammograms of Fe-N-C, (phen₂N₂)FeCl, and (OEP)FeCl recorded in the absence of O₂ provide insight into the redox potential of the metal center. For (OEP)Fe (FIG. 22, orange), we observe a broad redox feature with $E_{1/2}$ = 0.27 V (all potentials are

reported vs the reversible hydrogen electrode, RHE), similar to reported values for carbon-supported iron porphyrin complexes.^{112,133} For (phen₂N₂)Fe (FIG. 22, blue), we observe a reversible redox wave at 0.59 V. Based on the known Nernstian pH dependence of Fe(III/II) couples for adsorbed porphyrin complexes as well as the quasi-Nernstian behavior of the redox wave for (phen₂N₂)Fe, we assign these redox processes to the one-electron, one-proton reduction of Fe(III)-OH to Fe(II)-OH₂. For Fe-N-C (FIG. 22, black), we observe a large double layer capacitance, consistent with the high surface area of the material, and a pronounced redox wave at 0.63 V (FIG. 22). Other literature reports have observed waves for Fe-N-C materials at ~0.8 V, in line with the onset of ORR catalysis at Fe-N-C materials (see below) and so we attribute the wave we observe at 0.63 V to proton-coupled electron transfer (PCET) reactions of quinone and hydroxyl moieties on the Fe-N-C surface. We postulate that the actual Fe(III)-OH/Fe(II)-OH₂ redox process for Fe-N-C is obscured by the large double layer charging background in this high surface area material and the likely distribution of iron redox potentials in the heterogeneous material. We also note that some Fe redox centers may not engage in PCET reactivity and would, therefore, not be expected to display a redox wave. Nonetheless, the 0.32 V positive shift of the Fe redox couple for (phen₂N₂)Fe vs (OEP)Fe is consistent with the more electron withdrawing character of the pyridinic primary ligation sphere, which brings this model complex much closer in electronic character to the electropositive iron environments in Fe-N-C materials.

The observed Fe(III/II) redox waves result from only a fraction of the catalyst loaded into the dropcast film. The integrated charge in the Fe(III/II) redox waves of the (phen₂N₂)FeCl catalyst film corresponds to 7% of the total catalyst loading (FIG. 23). This contrasts with the (OEP)FeCl film, for which the Fe(III/II) wave integration corresponds to 43% of the total catalyst loading. We attribute this difference to the improved solubility of the porphyrin catalyst leading to better dispersion within the film. Nonetheless, these PCET redox potentials provide a good indication that the iron centers in (phen₂N₂)Fe are more electropositive than those in (OEP)Fe.

(Phen₂N₂)FeCl catalyzes ORR at lower overpotentials and with higher TOF values than (OEP)FeCl. (Phen₂N₂)FeCl is a potent catalyst for the oxygen reduction reaction. In O₂-saturated 0.1 M HClO₄, the reversible surface redox wave at 0.59 V (FIG. 24, black) is replaced by a large catalytic wave that displays an onset potential of 0.75 V (all onset potentials correspond to a current density of 0.1 mA cm⁻² and all electrochemical performance parameters are collected in FIG. 27) and reaches a current plateau at ~0.5 V

(FIG. 24, red). This catalytic wave spans the same potential range as the reversible redox feature in the absence of O₂ suggesting that ORR catalysis is mediated by the Fe(III/II) redox process (FIG. 24, inset). Catalytic activity is improved in basic media with an onset of 0.88 V in 0.1 M KOH (FIG. 25, a). The catalytic activity of (phen₂N₂)FeCl (FIG. 26, blue) is significantly greater than that of (OEP)FeCl (FIG. 26, orange), which displays onset potentials of 0.45 and 0.74 V in HClO₄ and KOH, respectively. Additionally, the unmetalated (phen₂N₂)H₂ ligand has activity comparable to the carbon background (FIG. 26, green) in acidic media with an onset potential of 0.34 V (FIG. 26, red) and activity slightly higher than background in alkaline media with an onset potential of 0.75 V, 130 mV negative of (phen₂N₂)FeCl (FIG. 25, a, and FIG. 28). Notably, the 0.3 V increase in ORR onset potential for (phen₂N₂)FeCl relative to (OEP)FeCl in acid is comparable to the 0.32 V positive shift in the Fe(III/II) redox potential. For homogeneous molecular iron porphyrins, TOF values typically track inversely with the Fe(III/II) redox potential. Yet, for (phen₂N₂)FeCl, the dramatic increase in Fe(III/II) potential does not seem to lead to a correlated decrease in ORR rate⁷² suggesting that (phen₂N₂)FeCl does not follow the same linear free-energy correlations observed for molecular porphyrin catalysts. The catalytic enhancement is also reflected in significantly increased per-site turnover frequencies (TOFs). TOF values in electron passed per site per second were extracted as a function of potential by dividing the current density by the integrated charge passed in the Fe(III/II) redox feature (FIG. 25, b, and FIG. 29, a). Remarkably, (phen₂N₂)FeCl displays a dramatically enhanced TOF that is 1400-fold higher than that of (OEP)FeCl in the activation-controlled region at 0.55 V in 0.1 M HClO₄ and 230-fold higher in the same region at 0.80 V in 0.1 M NaOH (FIG. 30). These observations establish that changing the primary coordination environment from pyrrolic to pyridinic leads to a dramatic enhancement in catalytic activity for ORR.

Although the catalytic performance of (phen₂N₂)FeCl is superior to (OEP)FeCl, it remains at a deficit to Fe-N-C. While the Fe(III/II) redox potential is difficult to discern for Fe-N-C, the positive shift of the Fe(III) peak in the XPS suggest that the iron centers in Fe-N-C are even more electropositive than the those in (phen₂N₂)FeCl and this may contribute to the higher onset potentials of 0.90 and 0.94 V observed for the Fe-N-C catalyst in acidic and alkaline media, respectively, (FIG. 26 and FIG. 25, a, black). Furthermore, unlike in (phen₂N₂)FeCl, the iron centers in Fe-N-C interact strongly with the delocalized band states of the N-doped graphitic carbon matrix and, indeed, a recent study on cobalt porphyrins

indicates that strong electron coupling to graphite can dramatically increase ORR activity relative to a porphyrin of identical local structure with weak coupling to the surface. Studies are ongoing to synthesize $(\text{phen}_2\text{N}_2)\text{FeCl}$ analogs that can be conjugated to graphitic carbon electrodes to directly examine the role of electronic coupling on ORR activity.

Notwithstanding, the fact that a discrete molecular complex such as $(\text{phen}_2\text{N}_2)\text{FeCl}$ displays an ORR onset within 150 mV of champion Fe-N-C materials suggests enormous opportunities for rational molecular design of highly active Fe-based ORR catalysts based upon pyridinic macrocyclic complexes.

Furthermore, $(\text{phen}_2\text{N}_2)\text{FeCl}$ displays high selectivity for the four-electron reduction of O_2 that is comparable to Fe-N-C and greater than that of $(\text{OEP})\text{FeCl}$. Using rotating ring disk electrode (RRDE) voltammetry (FIGs. 31 and 32) we determined the percent H_2O_2 produced as a function of applied potential for all three catalysts (FIG. 29, b and FIG. 33). For $(\text{phen}_2\text{N}_2)\text{FeCl}$, H_2O_2 production stabilizes rapidly, reaching values of <1% and 3% in acid and alkaline media at 0.40 V vs RHE, respectively (FIG. 29, b, and FIG. 33, blue). These values correspond to 3.99 and 3.95 electrons transferred in each condition, respectively, (FIG. 34). Indeed, in both acidic and alkaline media, the selectivity of $(\text{phen}_2\text{N}_2)\text{FeCl}$ in the transport-limited region surpasses that of Fe-N-C at the same potential (1% and 5% H_2O_2 in 0.1 M HClO_4 and 0.1 M NaOH , respectively, at 0.40 V). Further, in stark contrast to $(\text{phen}_2\text{N}_2)\text{FeCl}$, $(\text{OEP})\text{FeCl}$ displays significantly lower selectivity with 26% and 4% H_2O_2 in acidic and alkaline media, respectively, at the same potential of 0.40 V (FIG. 29, b, and FIG. 33, orange). Notably, for both $(\text{phen}_2\text{N}_2)\text{FeCl}$ and Fe-N-C, the hydrogen peroxide percentages increase in alkaline media and this may result from the action of less-selective non-metallic active sites capable of ORR in alkaline media. Indeed, for the metal-free $(\text{phen}_2\text{N}_2)\text{H}_2$ ligand supported on carbon, we observed significantly higher levels of H_2O_2 in alkaline media (17% at 0.40 V and a maximum of 26%, FIG. 35, b). Overall, these results highlight the ability of this tetrapyridinic Fe-N₄ coordination environment to facilitate selective O_2 -reduction pathways in both acidic and alkaline media. The similar trends in selectivity between this complex and Fe-N-C further support the notion that the $(\text{phen}_2\text{N}_2)\text{Fe}$ motif is an effective functional model of Fe-N-C catalysts.

Whereas Fe-N-C materials are relatively stable, we observe limited stability of the $(\text{phen}_2\text{N}_2)\text{FeCl}$ catalyst with activity decaying in acidic media over the course of several slow scan cyclic voltammograms (15–20 min). A similar deactivation is also observed for $(\text{OEP})\text{FeCl}$ and is well-documented in the literature. These observations highlight the

important role of the carbon framework in increasing the relative stability of Fe-N₄ sites in Fe-N-C materials against oxidative and protolytic decomposition induced by the acidic conditions and the presence of parasitic amounts of H₂O₂.¹⁴⁷ Indeed, we posit that extending the aromatic periphery around the (phen₂N₂)FeCl active site could enhance stability and provide a path towards the bottom-up synthesis of robust Fe-based ORR catalysts.

Table 6. Electrochemical Oxygen Reduction Onset and Selectivity of Fe-N-C and Vulcan-Supported Iron Macrocycle Complexes.

Complex ^a	Electrolyte	Onset potential (V) ^{b,c}	Max %H ₂ O ₂
Fe-N-C	0.1 M HClO ₄	0.91	~1
	0.1 M NaOH	0.91	~1
(phen ₂ N ₂)Fe ^{III} Cl	0.1 M HClO ₄	0.74	<4
	0.1 M NaOH	0.88	~1
(OEP)Fe ^{III} Cl	0.1 M HClO ₄	0.45	28
	0.1 M NaOH	0.74	13

^aOEP refers to 2,3,7,8,12,13,17,18-octaethylporphyrin. ^bV vs RHE. ^cDefined as the point where the current density surpasses 0.1 mV cm⁻².

ORR catalyzed by (phen₂N₂)FeCl (FIG. 10) demonstrated limited production of hydrogen peroxide (H₂O₂) in basic media (FIG. 12, d). The number of electrons transferred as a function of applied potential in acidic media is given in FIG. 11, and in basic media in FIG. 12, c. After reaching an appreciable current density, the number of electrons transferred remains near 4 for the subsequent potential range, with a maximum of about 4% H₂O₂ produced over a large overpotential regime, in good agreement with a range of pyrolyzed catalysts characterized by prominent D1 components in their respective Mössbauer spectra.

Density functional theory (DFT) was used to model the catalytic properties of porphyrin, (phen₂N₂), and two Fe-N₄ macrocycles with extended aromatic systems to represent the Fe-N-C materials for comparison. To evaluate catalytic activity and to compare to the experimental data, the binding energy of each of these catalysts with O₂ was calculated (see Table 7). Notably, (phen₂N₂)Fe binds O₂ more strongly than porphyrinFe by 0.25 eV, whereas the extended systems bind O₂ even more strongly. Such a trend in O₂ binding strength is in agreement with the observed trend in catalytic activity for a reaction

that is limited by the concentration of O₂ while the observed selectivity is similarly consistent with a catalyst possessing a more negative enthalpy of O₂-binding.

Table 7. Calculated Binding Energies of Small Molecules to PorphyrinFe^{II}, (phen₂N₂)Fe^{II} and Fe-N-C.

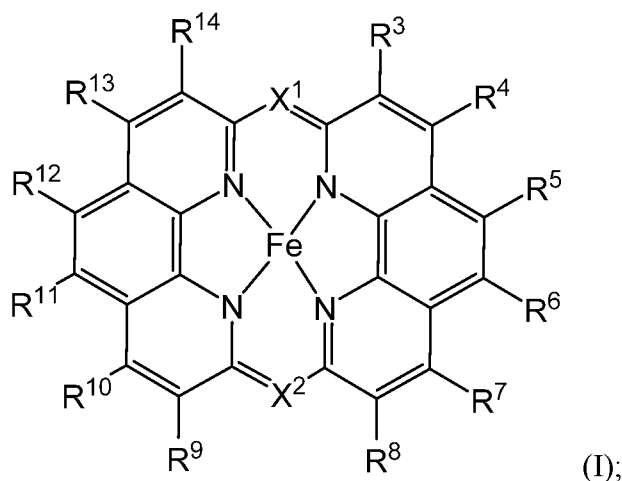
Catalyst	Binding Energy (eV)		
	O ₂	CO	CN ⁻
PorphyrinFe	-0.32	-0.73	-0.54
(phen ₂ N ₂)Fe	-0.57	-0.90	-0.68
(phen ₂ N ₂)Fe Extended 1 (Fe-N-C)	-0.91	-1.18	-0.78
(phen ₂ N ₂)e Extended 2 (Fe-N-C)	-0.76	-1.05	-0.79

The influence of CO and KCN on the catalytic waves was examined (FIGs. 13 and 14). In acidic media simultaneously sparged with CO and O₂, both partial and complete suppression of ORR activity for Fe-N-C and (phen₂N₂)FeCl was observed, respectively (FIG. 13). It can be reversed by removal of CO.⁴¹ Similar results are obtained in base. Given the ease of reversal, the ORR behavior can be attributed to a reduction in the relative partial pressure of O₂ in the cell when the solution is also being sparged with CO, as well as weakened CO binding at more anodic potentials where vFeCl and Fe-N-C catalyze ORR.⁴² ORR onset and limiting current values in the presence of KCN are diminished for both (phen₂N₂)FeCl and Fe-N-C, indicating a competition for the iron sites that is not completely reversed upon immersing the electrodes in fresh electrolyte.

The (phen₂N₂)Fe core developed here also allows for rational design of improved ORR catalysts. Unlike for Fe-N-C materials, synthetic derivatization of the (phen₂N₂)Fe architecture will uniformly modify all the active sites in the material, allowing for the extraction of molecular-level free-energy correlations. Moreover, borrowing from extensive studies of molecular porphyrin complexes, the secondary coordination sphere around the (phen₂N₂)Fe core can be tuned to generate three-dimensional surface active site environments that would be impossible to synthesize faithfully and selectively by traditional pyrolysis methods. Thus, the molecular model complex developed here provides a powerful platform with which to advance the synthesis and understanding of single-site heterogeneous electrocatalysts for critical energy conversion reactions

Compounds of the Invention

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof:



wherein

X^1 and X^2 are independently N, $C(R^{15})$, $(O^+)X^-$, or $(S^+)X^-$;

X^- is independently for each occurrence boron tetrafluoride, phosphorus tetrafluoride, phosphorus hexafluoride, alkylsulfonate, fluoroalkylsulfonate, arylsulfonate, bis(alkylsulfonyl)amide, bis(fluoroalkylsulfonyl)amide, bis(arylsulfonyl)amide, (fluoroalkylsulfonyl)(fluoroalkylcarbonyl)amide, halide, nitrate, nitrite, sulfate, hydrogensulfate, alkyl sulfate, aryl sulfate, carbonate, bicarbonate, alkyl carboxylate, aryl carboxylate, phosphate, hydrogen phosphate, dihydrogen phosphate, hypochlorite, or an anionic site of a cation-exchange resin;

Y^+ is Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , or $^+NR^{16}R^{17}R^{18}R^{19}$;

R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , and R^{14} are independently hydrogen, halogen, $-CN$, $-OR^{15}$, $-CO_2^-(Y^+)$, $-SO_3H$, $-SO_3^-(Y^+)$, $-NR^{16}R^{17}$, $-NO_2$, substituted or unsubstituted alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl, substituted or unsubstituted heteroaryl, substituted or unsubstituted heterocycloalkyl, haloalkyl, $-OC(O)R^{20}$, $-C(O)R^{20}$, $-C(O)OR^{20}$, $-C(O)NR^{21}R^{22}$, $-S(O)R^{23}$, or $-SO_2R^{23}$; and

R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , R^{20} , R^{21} , R^{22} , and R^{23} are independently hydrogen, haloalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl, substituted or unsubstituted heteroaryl, or substituted or unsubstituted heterocycloalkyl.

In certain embodiments, X^1 is N; and the compound of Formula I is a Bronsted conjugate acid or a quaternary (C₁-C₆)alkyl ammonium salt at X^1 .

In certain embodiments, X^2 is N; and the compound of Formula I is a Bronsted conjugate acid or a quaternary (C₁-C₆)alkyl ammonium salt at X^2 .

In certain embodiments, X^1 is N; X^2 is N; the compound of Formula I is a Bronsted conjugate acid or a quaternary (C₁-C₆)alkyl ammonium salt at X^1 ; and the compound of Formula I is a Bronsted conjugate acid or a quaternary (C₁-C₆)alkyl ammonium salt at X^2 .

In certain embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein X^1 is C(R¹⁵).

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein X^2 is C(R¹⁵).

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein X^1 is C(R¹⁵); and X^2 is C(R¹⁵).

In other embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein X^1 is N.

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein X^2 is N.

In other embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein X^1 is N; and X^2 is N.

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein X^1 is (O⁺)X⁻ or (S⁺)X⁻.

In certain embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein X^2 is (O⁺)X⁻ or (S⁺)X⁻.

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein X^1 is (O⁺)X⁻ or (S⁺)X⁻; and X^2 is (O⁺)X⁻ or (S⁺)X⁻.

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein R¹⁵ is hydrogen.

In other embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein R¹⁵ is substituted or unsubstituted alkyl. Alternatively, R¹⁵ is substituted or ituted cycloalkyl. In some instances, R¹⁵ is substituted or unsubstituted aryl. In

certain embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein R^{15} is substituted or unsubstituted heteroaryl.

In some embodiments, X^1 is $C(R^{15})$, $(O^+)X^-$, or $(S^+)X^-$.

In some embodiments, X^2 is $C(R^{15})$, $(O^+)X^-$, or $(S^+)X^-$.

In some embodiments, each of R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , and R^{14} is hydrogen.

In some embodiments, each of R^4 , R^7 , R^{10} , and R^{14} is phenyl.

In some embodiments, R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , and R^{14} are hydrogen; X^1 is N; and X^2 is N.

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein at least one of R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , and R^{14} is not hydrogen.

In certain embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein at least two of R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , and R^{14} are not hydrogen.

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein at least three of R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , and R^{14} are not hydrogen.

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein at least four of R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , and R^{14} are not hydrogen.

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , and R^{14} are hydrogen; and X^1 is $C(R^{15})$, $(O^+)X^-$, or $(S^+)X^-$.

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , and R^{14} are hydrogen; X^1 is $C(R^{15})$, $(O^+)X^-$, or $(S^+)X^-$; and X^2 is $C(R^{15})$, $(O^+)X^-$, or $(S^+)X^-$.

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , and R^{14} are hydrogen; and X^1 is $C(R^{15})$.

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , and R^{14} are hydrogen; X^1 is $C(R^{15})$; and X^2 is $C(R^{15})$.

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , and R^{14} are hydrogen; and X^1 is $(O^+)X^-$ or $(S^+)X^-$.

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , and R^{14} are hydrogen; X^1 is $(O^+)X^-$ or $(S^+)X^-$; and X^2 is $(O^+)X^-$ or $(S^+)X^-$.

In some embodiments, the disclosure relates to a compound of Formula I or a salt thereof, wherein R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , and R^{14} are hydrogen; X^1 is N; and X^2 is N.

Methods of Oxygen Reduction

In some embodiments, the disclosure relates to a composition comprising a compound of Formula I or a salt thereof and a support material; wherein the compound is in contact with the support material.

In some embodiments, the disclosure relates to a composition wherein the support material comprises carbon.

In some embodiments, the disclosure relates to a composition wherein the support material comprises carbon powder.

In some embodiments, the disclosure relates to a composition wherein the support material comprises carbon black (CB), multi-walled carbon nanotubes (MWCNT), graphene oxide (GO), or reduced graphene oxide (rGO).

In some embodiments, the disclosure relates to a composition wherein the compound is adsorbed on the support material.

In some embodiments, the disclosure relates to a cathode catalyst, comprising a compound of Formula I or a salt thereof or a composition comprising a compound of Formula I or a salt thereof.

In some embodiments, the disclosure relates to a fuel cell, comprising a cathode

catalyst comprising a compound of Formula I or a salt thereof or a composition comprising a compound of Formula I or a salt thereof.

In some embodiments, the disclosure relates to a method of reducing oxygen, comprising:

in an electrochemical device, applying current to a mixture comprising an aqueous medium, hydrogen gas, oxygen gas, and a compound of Formula I or a salt thereof or a composition comprising a compound of Formula I or a salt thereof.

In some embodiments, the disclosure relates to a method of reducing oxygen, wherein the aqueous medium is an alkaline medium.

In some embodiments, the disclosure relates to a method of reducing oxygen, wherein the electrochemical device is an anion-exchange membrane fuel cell or an alkaline metal-air battery.

In some embodiments, the disclosure relates to a method of reducing oxygen, wherein the aqueous medium is an acidic medium.

In some embodiments, the disclosure relates to a method of reducing oxygen, wherein the electrochemical device is a proton-exchange membrane fuel cell.

EXAMPLES

Although methods and materials similar or equivalent to those described herein can be used in the practice of the present invention, suitable methods and materials are described below. The invention is further described in the following examples, which do not limit the scope of the invention described in the claims.

General Synthetic Considerations

Where indicated, synthetic procedures were carried out under an inert atmosphere in a nitrogen-filled glovebox. All other synthetic transformations were carried out on the benchtop without effort to exclude dioxygen or moisture. Anhydrous 1,10-phenanthroline (99%), 1,3-dibromopropane (98%), *tert*-butanol (99%) and phosphorus pentachloride (98%) were obtained from Alfa Aesar. Potassium *tert*-butoxide (97%) and phosphoryl chloride (99%) were obtained from TCI and Sigma Aldrich, respectively. Compressed anhydrous ammonia (99.995%) was purchased from Airgas. *N,N*-dimethylformamide was deoxygenated and dried using a Glass Contour System (SG Water USA, Nashua, NH) and

stored in the glovebox over 4 Å molecular sieves. D₂O, CDCl₃ and *d*-TFA were purchased from Sigma-Aldrich and Cambridge Isotope Laboratories and used without further purification. 2, 3, 7, 8, 12, 13, 17, 18-Octaethyl-21*H*, 23*H*-porphine iron(III) chloride (OEP-FeCl) was purchased from Frontier Scientific. OEP-FeCl was used without further purification. Routine NMR spectra were recorded on Varian Mercury 300, Bruker Avance III 400 and Varian Inova 500 spectrometers. Chemical shifts for ¹H and ¹³C{¹H} spectra are reported in ppm downfield of TMS, with spectra referenced using the chemical shifts of the solvent residuals. Spectra collected in *d*-TFA were referenced to a benzene solvent residual by including a small capillary of C₆D₆ in the sample tube. UV-visible spectra were measured in a 1-cm quartz cell on a Varian Cary 50 monochromatic spectrophotometer. MALDI-TOF mass spectra were obtained using a Bruker Omnisflex instrument operating in reflectron mode, and the peaks reported are the mass number of the most intense peak in the isotope envelopes. Samples consisted of mixtures of analyte with 1,4-bis(5-phenyl-2-oxazolyl)benzene (POPOP) as a desorption matrix. In all cases, the observed isotope patterns were in good agreement with calculated ones. Elemental analyses were performed by Robertson Microlit Laboratories (Ledgewood, NJ).

Compounds **2-4** were obtained according to the procedures of Guo and coauthors⁴³ with several modifications: Compound **2** was synthesized using toluene as the solvent. Compound **3** was prepared using the modified workup described by Song *et al.*⁴⁴ The workup procedure for compound **4** was simplified by decomposing the POCl₃ solvent with aqueous ammonium hydroxide (30%) to a pH greater than 8 and filtering the resulting precipitate. The solid was washed with water, and dried in a 60 °C oven.

General Electrochemical Methods

i. Homogeneous. *N,N*-dimethylformamide previously treated as described above was stored in the glovebox before use for the preparation of all non-aqueous electrolytes. Trifluoroacetic acid (ReagentPlus® 99%) and tetrabutylammonium hexafluorophosphate (99%) were obtained from Sigma Aldrich. Thallium triflate (99%) was purchased from Strem Chemicals and used as received. [TBA][PF₆] was recrystallized from EtOH and stored in a 60°C oven before use. [DMF-H][OTf] was synthesized by a known procedure⁴⁶ and stored in the glovebox until use. In all cases, a custom Ag/AgCl pseudoreference electrode was used, constructed from a Ag/AgCl wire placed in a glass housing filled with 0.1 M [TBA][PF₆] in DMF and isolated from the bulk solution by a Vycor® frit. The experimental potentials measured against the pseudoreference electrode were adjusted to the Fc/Fc⁺ redox couple by

spiking the electrolyte with a small quantity of ferrocene. In all cases glassy carbon rod electrodes were used as both the cathode and anode. *See* FIG. 15.

Caution: Thallium is extremely toxic and is easily absorbed through the skin, particularly in the presence of a solvent like DMF. Handle with care. We elected to use TlOTf rather than a more common halide abstraction agent such as AgOTf due to the fact that the Tl redox couple is found at more cathodic potentials and is therefore less likely to convolute a cyclic voltammetry measurement.

ii. Heterogeneous. Sodium hydroxide (99.99%, semiconductor grade), potassium ferricyanide (ACS grade) and potassium sulfate (99.99%, semiconductor grade) were obtained from Sigma Aldrich and used as received. 5 wt% perfluorinated Nafion® resin solution was obtained from Ion Power Inc. Aqueous electrolyte solutions were prepared with deionized water purified to a resistivity of 18.2 M Ω -cm using a MilliQ water purification system (Millipore Corporation). Monarch 1300 and Vulcan VXC72R carbon powders were obtained from Cabot Corporation and used as received. Glassy carbon disk electrodes were obtained from Pine Research Instrumentation, Inc. Hg/HgO and Hg/Hg₂SO₄ reference electrodes were obtained from CHI instruments, Inc. A titanium mesh was used as the counter electrode for all electrochemical experiments. The titanium counter was constructed of titanium wire (99.9%) and titanium gauze (40 mesh) obtained from Alfa Aesar and was treated with aqua regia prior to use.

All electrochemical experiments were conducted at ambient temperature using a Biologic VSP 16-channel potentiostat and a three-electrode electrochemical cell. In all cases, the counter electrode was isolated from the working compartment by a counter compartment equipped with a porous glass frit. Hg/HgO and Hg/Hg₂SO₄ reference electrodes were used for all experiments conducted in alkaline and acidic aqueous electrolytes, respectively. The Hg/HgO reference was stored in 3 M NaOH solution between measurements. Electrode potentials measured in aqueous alkaline media were converted to the reversible hydrogen electrode (RHE) scale using the following relationship: $E(\text{RHE}) = E(\text{Hg}/\text{HgO}) + 0.094 \text{ V} + 0.059 \cdot (\text{pH}) \text{ V}$. The Hg/Hg₂SO₄ electrode was stored in saturated K₂SO₄ solution between measurements. Electrode potentials measured in aqueous acidic media were converted to the RHE scale using $E(\text{RHE}) = E(\text{Hg}/\text{Hg}_2\text{SO}_4) + 0.65 \text{ V} + 0.059 \cdot (\text{pH}) \text{ V}$.

Routine electrochemical measurements were performed at a 5 mm diameter glassy carbon disk electrode rotated at 2000 RPM. All scan rates were 5 mV/s to allow for adequate equilibration between the bulk solution and outer Helmholtz plane. Cyclic and linear sweep

voltammograms were started from the open circuit potential and swept in the cathodic direction. All experiments were run without iR compensation due to negligible iR losses in the electrolytes used in this study. Solutions were sparged for 10 minutes before the initial experiment with either N_2 or O_2 and for another 10 minutes when changing between solubilized gases. During an experiment, the headspace of the cell was continually flushed with the working gas to minimize solution contamination by atmospheric gases. All experiments were conducted using 10 μL of ink was dropcast on a polished RDE, except where noted. Catalytic onset potentials were taken to be the potential at which the observed current density was equivalent to $-100 \mu\text{A cm}^{-2}$.

a. Preparation of Carbon Inks. Inks for use in electrochemical studies are obtained by suspending 1 mg/mL catalyst (either porphyrin- or (phen₂N₂)-based) in 2.5 mg/mL Vulcan VXC72R carbon. DCM, EtOH and 5 wt% Nafion solution are added sequentially in a ratio of 7:2:1. The resulting mixture is sonicated for 16 minutes to give the product ink. Inks were usually produced in 1 mL batches. Note that superior results in terms of carbon powder dispersion and ORR activity are obtained when DCM is added to the solid precursor mixture first followed by EtOH and Nafion solution.

b. Rotating ring-disk electrode (RRDE) voltammetry. RRDE was performed with a Pine rotator using a ChangeDisk tip. RRDE experiments conducted in acid were performed with a platinum ring while experiments conducted in base were performed with a gold ring.⁴⁴ The Pt and Au rings were cleaned by cyclic voltammetry at 50 mV s^{-1} over potential ranges of 1 to -0.8 V and 1.1 to -0.7 V, respectively, vs the $\text{Hg}/\text{Hg}_2\text{SO}_4$ reference in 0.1 M HClO_4 . The potential was swept over this range until the cyclic voltammograms overlaid exactly.

The proportion of H_2O_2 produced during ORR was quantified using the following relationship:⁴⁵

$$\% \text{H}_2\text{O}_2 = \frac{100(\frac{2i_{ring}}{N})}{i_{disk} + (\frac{i_{ring}}{N})} \quad (1)$$

In this case, i_{ring} and i_{disk} are the currents at the ring and disk electrodes, respectively and N is the collection efficiency. The number of electrons transferred as a function of applied potential was calculated using equation 2:⁴⁶

$$n_{e-} = \frac{4i_{disk}}{i_{disk} + \left(\frac{i_{ring}}{N}\right)} \quad (2)$$

The collection efficiency constant was calculated at the end of each experimental set under a given set of conditions by examining the Fe(III/II) couple of a suitable redox reagent via chronoamperometry or cyclic voltammetry where the collection efficiency is defined as the ratio of i_{ring} to i_{disk} . Typical collection efficiency values were in the range of 18-22%. Collection efficiency measurements were conducted using a blank glassy carbon disk and clean ring. $Fe_2(SO_4)_3$ and $K_3Fe(CN)_6$ were used as the redox agents for the collection efficiency measurements in acid and base, respectively.

Zero-Field ^{57}Fe Mössbauer spectroscopy and curve fitting. Zero-field ^{57}Fe Mössbauer spectra were measured with a constant acceleration spectrometer (SEE Co., Minneapolis, MN) at 90 K. Solid samples (20-30 mg for molecular samples and 120 mg for Fe-N-C) were prepared by mixing each sample powder with Paratone-N oil. With the exception of the $(phen_2N_2)FeCl$ sample, each sample was prepared outside the glovebox. The $(phen_2N_2)FeCl$ sample was prepared similarly except the sample preparation process was carried out inside a nitrogen-filled glovebox and the sample was frozen with liquid nitrogen before handling outside the glovebox. All isomer shifts are reported relative to α -Fe metal at 298 K. All data were processed, fitted, and analyzed using an in-house software package for IGOR Pro 6 (Wavemetrics, Lake Oswego, OR).

X-ray photoelectron spectroscopy and curve fitting. X-ray photoelectron spectroscopy experiments were performed on ThermoFisher Aluminum K Alpha+ (ESCA) or ThermoFisher Nexsa X-ray spectrometer systems with monochromatic aluminum K_{α} X-ray sources (1486.68 eV). Samples for analysis were prepared by distributing a small amount of Au powder (for referencing) on conductive carbon tape and spreading the analyte on top. The analyte was mixed with the Au powder to allow for simultaneous detection of analyte and the Au powder. All experiments were run with the flood gun on to prevent sample charging. All data were collected using a 400 μm , 72 W focused X-ray beam at a base pressure of 2×10^{-7} millibar or lower. Survey scans were collected at a pass energy of 200 eV and step size of 1 eV. High resolution scans were collected with a pass energy of 50 eV and a step size of 0.1 eV. All data were analyzed with the Thermo Advantage software package (v5.987). The Au 4f_{7/2} peak arising from the Au powder was assigned an energy of 84.0 eV and used as an internal binding energy reference for all spectra. In all cases the recorded

spectral data was not modified with a smoothing algorithm. High-resolution spectra were fit by application of a Shirley-type (Smart) background and Gaussian/Lorentzian line-shapes of 30% Gaussian shape. The Simplex fitting algorithm was used in all cases. This procedure was used to generate the data in FIG. 19.

X-ray absorption spectroscopy.

X-ray absorption spectroscopy (XAS) experiments were performed at the 10-BM beamline at the Advanced Photon Source (APS) at Argonne National Laboratory. All measurements were performed at the Fe K edge (7.112 keV) in transmission mode in fast scan from 250 eV below the edge to 550 eV above the edge. Samples were pressed into a stainless-steel sample holder and placed in a sample cell. The cell was sealed and purged with He at room temperature. The data were interpreted using WinXAS 3.1 software to find the coordination number and bond distance using standard procedures. The phase and amplitude functions for Fe-N and Fe-O were extracted from theoretical Feff6 calculations. The Fe foil (CN=8, R=2.54 Å) was used as a reference to calibrate the S_0^2 , which was 0.64. Theoretical phase and amplitude files were created for the Fe-N (CN=1, R=1.94 Å) and Fe-O (CN=1, R=1.99 Å) scattering pairs. Least squared fits of the first shell of r- space and isolated q- space were performed on the k^2 weighted Fourier transform data over the range 2.71 to 10 Å⁻¹ in each spectrum to fit the magnitude and imaginary components.

Computational Details

All DFT calculations were performed using the ab-initio software package Q-Chem,⁴⁸ using the meta-hybrid functional TPSSH⁴⁹ and the basis set 6-31+G*.⁵⁰⁻⁵² To model solvation, the implicit solvation model IEF-PCM with a dielectric constant of 78.4 was used.⁵³ All molecular images were generated using the software package VESTA.⁵⁴

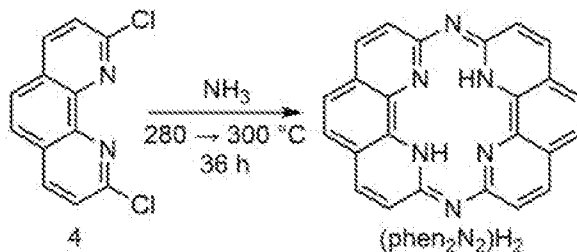
The geometry of (phen₂N₂)Fe, porphyrinFe, and both material analogues were optimized with spin states $m_s = 0, 1$, and 2. It was determined that the most stable spin state with our method is $m_s = 1$, as has previously been noted for porphyrinFe.⁵⁵ The geometry of each catalyst was optimized with O₂, CN⁻, and CO bound to the iron atom of (phen₂N₂)Fe with various spin states, and it was determined that $m_s = 0$ is the most stable spin state. For O₂, it was necessary to break spin symmetry and obtain the lower energy anti-ferromagnetic ground singlet state, for which constrained-DFT was used to generate an initial guess for a subsequent unrestricted calculation.⁵⁶

Example 1. Synthesis of $(phen_2N_2)H_2$ and $(phen_2N_2)FeCl$.

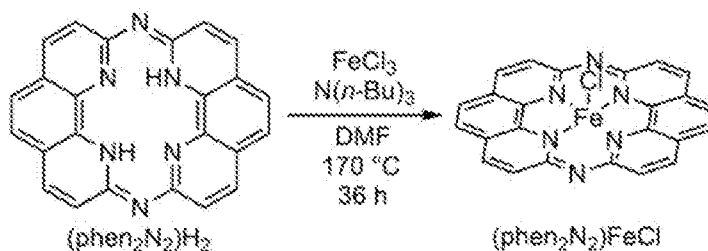
Compound **2** was synthesized via alkylation of 1,10-phenanthroline using an excess of 1,3-dibromopropane in refluxing toluene. Briefly, 10.787 g (59.86 mmol) 1,10-phenanthroline was suspended in 105 mL toluene. The mixture was stirred and heated to 70 °C and, subsequently, 28 mL (55.47 g, 275 mmol, 4.59 equiv.) 1,3-dibromopropane was added. The temperature was increased to 120 °C and the mixture was refluxed for 4 hours. After allowing the reaction vessel to cool, the mixture was filtered and washed with hexanes to yield 18.688 g (82%) of compound **2** as a yellow powder. Observed NMR peaks in D₂O matched the literature.⁴³

Compound **3** was prepared using the modified workup described by Song *et al.*⁴ 5.061 g (13.24 mmol) of compound **2** was suspended in 85 mL *tert*-butanol and sonicated for 15 minutes. The mixture was then stirred while 6.026 g (53.7 mmol, 4.06 equiv.) KO^tBu was added in small portions over the course of 15 minutes. The reaction mixture was then heated to 40 °C and stirred for 12 hours. The solvent was removed by rotary evaporation and the crude material was suspended in 100 mL of water. The product was extracted with 100 mL of chloroform and 5% methanol by volume was added to the chloroform solution. The mixture was then filtered through a plug of silica on a glass frit and the silica was washed with chloroform until the eluant was colorless. The combined washings were concentrated to dryness by rotary evaporation to yield 1.746 g (52%) of compound **3** as a brown solid. The observed NMR peaks in CDCl₃ matched those reported in the literature.⁴³

Compound **4** was synthesized via treatment of compound **3** with PCl₅ in POCl₃. Under inert atmosphere, a mixture of 1.916 g (7.60 mmol) compound **3** and 3.326 g (15.97 mmol) PCl₅ was suspended in 40 mL POCl₃. The mixture was then refluxed under inert atmosphere for 14 hours. After cooling to room temperature, the POCl₃ solvent and unreacted PCl₅ were quenched and the resulting mixture was neutralized with aqueous ammonium hydroxide (30%) to a pH >8. After neutralization, the resulting precipitate was filtered. The solid was washed with water and dried overnight in an oven to yield 1.801 g (95%) of compound **4** as a light brown powder. NMR peaks in CDCl₃ matched those given in the literature.⁴³



3bH,10bH-1,14:7,8-Diethenotetrapyrido[2,1,6-*de*:2',1',6'-*gh*:2'',1'',6''-*kl*:2''',1''',6'''-*na*][1,3,5,8,10,12]hexa-azacyclotetradecine, **(phen₂N₂)H₂**. 0.5467 g (2.19 mmol) 2,9-dichlorophenanthroline is added to a cylindrical glass insert and enclosed in a Parr bomb at room temperature. The bomb was purged with nitrogen for 10 minutes before being pressurized with anhydrous ammonia at 114 PSI. The bomb was then immersed in a bed of aluminum beads and brought to 300 °C using a heating mantle over 24 hours. After heating for a further 5 hours, the bomb is allowed to return to room temperature. The residual ammonia is vented and the crude product is dissolved in a mixture of acetic acid and methanol and stirred for 30 minutes. The mixture is basified with 4M NaOH before the mixture is stirred for an additional 12 hours. The precipitate is filtered and sequentially washed with 100 mL each of ethanol and chloroform before being dried at 60 °C for 12 hours. The filtrate is concentrated *in vacuo* and heated to 300 °C under inert atmosphere for a further 24 hours in a 500 mL round bottom flask affixed to a reflux condenser. After cooling to room temperature, the solid derived from the filtrate is treated with an identical dissolution, precipitation and washing sequence as before to yield a second crop. 0.2797 g (0.506 mmol, 66% combined yield) of (phen₂N₂)H₂ is isolated as a brown solid. ¹H NMR (C₆D₆ in *d*-TFA): δ 9.41 (d, 4H, 10 Hz), 8.76 (s, 4H), 8.49 (d, 4H, 10 Hz). MALDI-MS (POPOP matrix): *m/z* 386.42 [M]⁺ Anal. Calcd for (phen₂N₂)H₂•H₂O (C₂₄H₁₆N₆O₁): C, 71.28; H, 3.99; N, 20.78. Found: C, 70.93; H, 3.47; N, 21.12.



1,14:7,8-Diethenotetrapyrido[2,1,6-*de*:2',1',6'-*gh*:2'',1'',6''-*kl*:2''',1''',6'''-*na*][1,3,5,8,10,12]hexa-azacyclotetradecine iron(III) chloride, **(phen₂N₂)FeCl**. 0.0600 g (0.155 mmol) (phen₂N₂)H₂ is added to a pressure tube containing a stir bar in the glovebox.

0.0358 g (0.221 mmol, 1.42 equiv.) FeCl_3 and 0.221 mL (0.930 mmol, 6.00 equiv.) Bu_3N are added to the vessel followed by 7 mL DMF. The tube is sealed and removed from the glovebox before being heated to 170 °C for 36 hours with vigorous stirring. The temperature is allowed to return to ambient levels and the mixture is diluted with 20 mL DCM under inert atmosphere. The mixture is then cooled overnight at -38 °C and the resulting precipitate filtered and washed with ether and DCM to yield 54 mg (73%) $(\text{phen}_2\text{N}_2)\text{FeCl}$. HR MALDI-TOF (POPOP matrix): m/z 440.1197 ($M - \text{Cl}$, calc. for $\text{C}_{24}\text{H}_{16}\text{FeN}_6$: 440.0473).

Example 2. Synthesis of Fe-N-C.

Fe-N-C was synthesized by a hybrid method adapted from previously published procedures.^{57,58} 19.4 mg (0.111 mmol) $\text{Fe}(\text{OAc})_2$, 206.3 mg (1.14 mmol) 1,10-phenanthroline and 803.5 mg (3.53 mmol) ZIF-8 MOF are mixed together in an agate mortar for 15 minutes. To remove excess water and oxygen, the prepyrolysis mixture was subjected to vacuum for 30 minutes at 90 °C followed by a further 12 hours at room temperature. 855.7 mg of the precatalyst powder is weighed into an alumina boat and loaded into a single-zone alumina tube furnace. The tube furnace is sealed and placed under vacuum briefly before being continuously purged with argon. The furnace is heated to 1000 °C at a ramp rate of 10 °C min^{-1} and maintained at 1000 °C for 60 minutes. The furnace is allowed to return to room temperature and the system is evacuated before being continuously purged with 5% hydrogen in argon. The furnace is ramped to 800 °C at a rate of 10 °C min^{-1} and maintained at 800 °C for 30 minutes before being allowed to return to room temperature. The product Fe-N-C is sonicated in 30 mL of 0.1 M H_2SO_4 for 60 minutes. Afterwards, the product is filtered and washed with water until the eluant pH is neutral. After washing with acetone to remove excess water, the product is dried overnight at 60 °C to yield 219.2 mg of Fe-N-C.

Example 3. Synthesis of $(\text{ph}_4\text{phen}_2\text{N}_2)\text{FeCl}$.

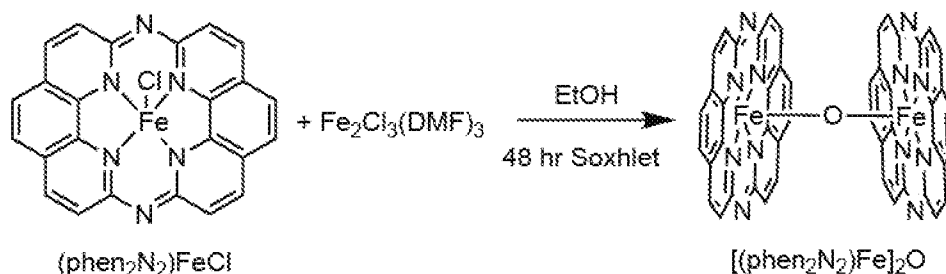
$(\text{Ph}_4\text{phen}_2\text{N}_2)\text{FeCl}$ was synthesized according to the route depicted in Scheme 1.

Synthesis of **$(\text{ph}_4\text{phen}_2\text{N}_2)\text{H}_2$** . 17.3 mg (0.0477 mmol) 2,9-diaminobathophenanthroline is added to a 50 mL flask containing a stir bar. 17.3 mg (0.047 mmol, 0.99 equiv.) 2,9-difluorobathophenanthroline and 0.704 g (5.1 mmol, 107 equiv.) potassium carbonate are added to the flask. 40 mL DMF is added and the mixture is degassed and the yellow mixture is stirred for 48 hours at 160 °C. After cooling to room

temperature, the mixture is poured into 100 mL distilled water. The resulting precipitate is collected by centrifugation and dried in a 60 °C oven. Chromatography in 5% methanol in dichloromethane on silica gel gives the title compound as a yellow solid. ^1H NMR (CDCl_3): δ 7.66 (s, 4H), 7.64 (dd, 8H, 8, 2 Hz), 7.58-7.52 (m, 16H). MALDI-MS (POPOP matrix): m/z 690.624 ($[\text{M}]^+$ calc. for $\text{C}_{24}\text{H}_{14}\text{N}_6$: 690.253).

Synthesis of **(ph₄phen₂N₂)FeCl**. 21.5 mg (0.0312 mmol) (ph₄phen₂N₂)H₂ is added to a 25 mL flask containing a stir bar and is dissolved in 4 mL dimethylacetamide. 15.3 mg (0.077 mmol, 2.47 equiv.) $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 0.2 mL (0.145 g, 1.43 mmol, 46 equiv.) triethylamine are added and the mixture is stirred at 155 °C for 4 hours. After cooling the mixture to room temperature, the contents are poured onto ice. 4 mL of 6 M aqueous HCl is added and the mixture is stirred at room temperature for 14 hours. The mixture is extracted repeatedly with dichloromethane. The organics are combined and concentrated to dryness on the rotary evaporator. During the process of removing the solvent, heptane is added to help remove trace dimethylacetamide. Afterwards, the brown solid is placed in a 100 °C oven for several hours. 23 mg (95%) (ph₄phen₂N₂)FeCl is obtained as a brown powder. MALDI-TOF (POPOP matrix): m/z 744.583 ($[\text{M} - \text{Cl}]^+$, calc. for $\text{C}_{48}\text{H}_{28}\text{FeN}_6$: 744.177), 779.571 ($[\text{M}]^+$, calc. for $\text{C}_{48}\text{H}_{28}\text{ClFeN}_6$: 779.141).

Example 4. Synthesis of $[(\text{phen}_2\text{N}_2)\text{Fe}]_2\text{O}$ and $[(\text{OEP})\text{Fe}]_2\text{O}$.

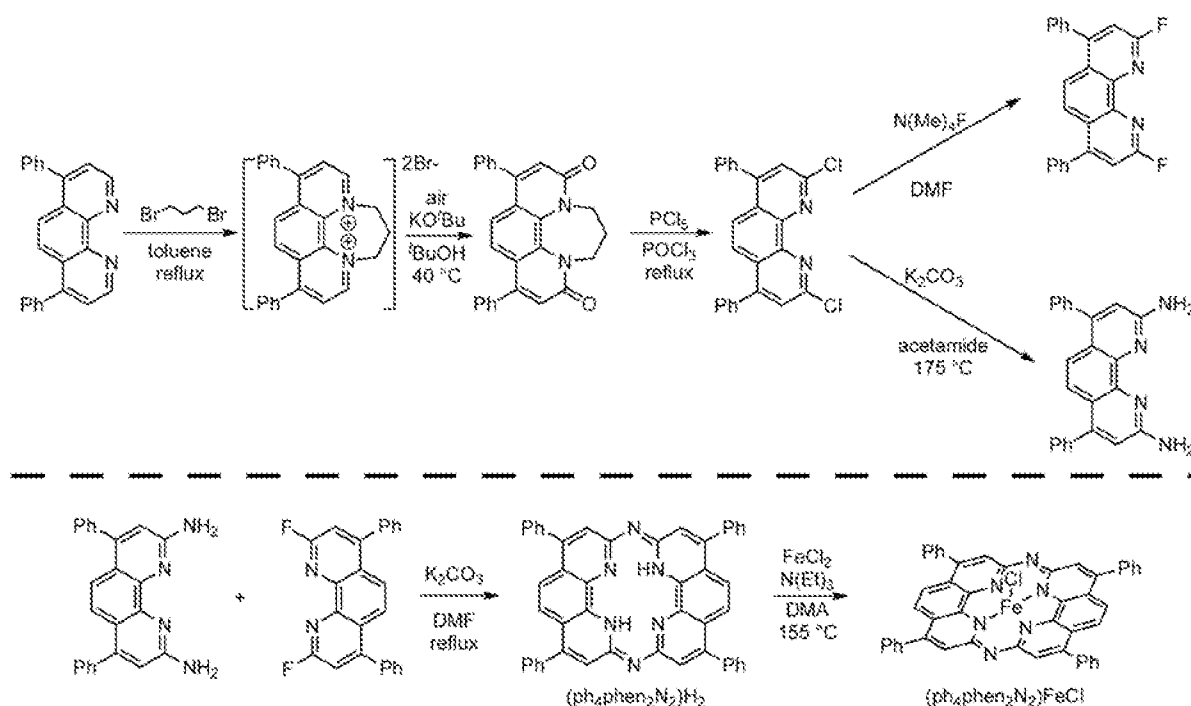


Synthesis of $[(\text{phen}_2\text{N}_2)\text{Fe}]_2\text{O}$. (μ -Oxo)bis[(1,14:7,8-Diethenotetrapyrido[2,1,6-de:2',1',6'-gh:2'',1'',6''-kl:2''',1''',6'''-na][1,3,5,8,10,12]hexa-azacyclotetradecine)iron(III)], **$[(\text{phen}_2\text{N}_2)\text{Fe}]_2\text{O}$** . In a typical preparation, a sample of $(\text{phen}_2\text{N}_2)\text{FeCl}$ was placed in a cellulose extraction thimble and loaded into a Soxhlet apparatus. After placing the apparatus under inert atmosphere by purging extensively with argon, the sample was washed continuously with hot ethanol for 48 hours. Afterwards, the sample was removed from the Soxhlet apparatus and dried in an oven overnight to remove trace water and volatile solvents. XPS N:Fe ratio: 6.3:1. ^{57}Fe Mössbauer (90 K): $\delta = 0.45 \text{ mm s}^{-1}$, $|\Delta E_Q| = 0.97 \text{ mm s}^{-1}$. HR MALDI-TOF (POPOP matrix): m/z 440.0975 ($[\text{M} - \text{C}_{24}\text{H}_{12}\text{FeN}_6\text{O}]^+$, calc.

for $C_{24}H_{12}FeN_6$: 440.0473). A satisfactory elemental analysis for $[(phen_2N_2)Fe]_2O$ could not be obtained due the presence of trace impurities, which were presumably carried through the metalation and Soxhlet procedures. Similar solubility issues as $(phen_2N_2)FeCl$ above trap trace impurities which are not easily removed by washing.

Synthesis of $[(OEP)Fe]_2O$. (μ -Oxo)bis[(octaethylporphinato)iron(III)], $[(OEP)Fe]_2O$. Octaethylporphinatoiron(III) chloride dissolved in CH_2Cl_2 was vigorously shaken in a separatory funnel with 2 M NaOH. After separating the layers, the organic layer was washed with water, dried over $MgSO_4$ and filtered. After washing the $MgSO_4$ with CH_2Cl_2 , the combined organic layers were concentrated to dryness, resulting in a brown microcrystalline solid which was then dried at 60 °C for several hours. The Fe-O-Fe unit was identified by infrared spectroscopy with characteristic bands at 870 and 832 cm^{-1} . These observed values are in line with those reported in the literature for $[(OEP)Fe]_2O$.⁸ Mössbauer (90 K): $\delta = 0.41 \text{ mm s}^{-1}$, $|\Delta E_Q| = 0.67 \text{ mm s}^{-1}$.

Scheme 1. Synthetic route to $(ph_4phen_2N_2)H_2$ and $(ph_4phen_2N_2)FeCl$ from 2,9-dichloro-1,10-phenanthroline.



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INCORPORATION BY REFERENCE

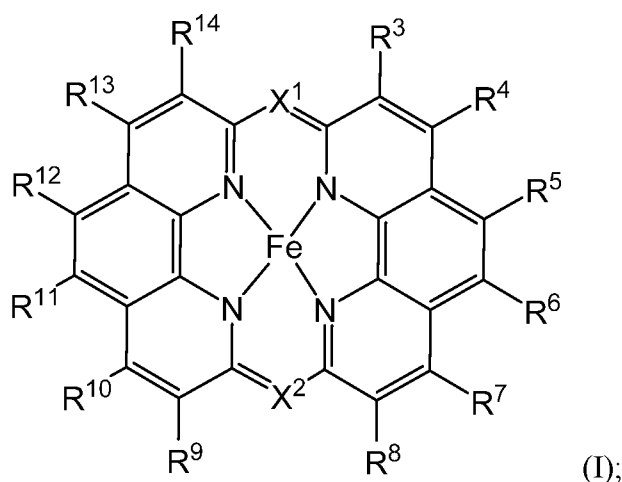
All of the U.S. patents and U.S. patent application publications cited herein are hereby incorporated by reference. In case of conflict, the present specification, including definitions, will control.

EQUIVALENTS

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. Such equivalents are intended to be encompassed by the following claims.

What is claimed is:

1. A compound of Formula I or a salt thereof:



wherein

X^1 and X^2 are independently N, $C(R^{15})$, $(O^+)X^-$, or $(S^+)X^-$;

X^- is independently for each occurrence boron tetrafluoride, phosphorus tetrafluoride, phosphorus hexafluoride, alkylsulfonate, fluoroalkylsulfonate, arylsulfonate, bis(alkylsulfonyl)amide, bis(fluoroalkylsulfonyl)amide, bis(arylsulfonyl)amide, (fluoroalkylsulfonyl)(fluoroalkylcarbonyl)amide, halide, nitrate, nitrite, sulfate, hydrogensulfate, alkyl sulfate, aryl sulfate, carbonate, bicarbonate, alkyl carboxylate, aryl carboxylate, phosphate, hydrogen phosphate, dihydrogen phosphate, hypochlorite, or an anionic site of a cation-exchange resin;

R^3 , R^4 , R^5 , R^6 , R^7 , R^8 , R^9 , R^{10} , R^{11} , R^{12} , R^{13} , and R^{14} are independently hydrogen, halogen, $-CN$, $-OR^{15}$, $-CO_2^-(Y^+)$, $-SO_3H$, $-SO_3^-(Y^+)$, $-NR^{16}R^{17}$, $-NO_2$, substituted or unsubstituted alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl, substituted or unsubstituted heteroaryl, substituted or unsubstituted heterocycloalkyl, haloalkyl, $-OC(O)R^{20}$, $-C(O)R^{20}$, $-C(O)OR^{20}$, $-C(O)NR^{21}R^{22}$, $-S(O)R^{23}$, or $-SO_2R^{23}$;

Y^+ is Li^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+} , or $+NR^{16}R^{17}R^{18}R^{19}$;

and

R^{15} , R^{16} , R^{17} , R^{18} , R^{19} , R^{20} , R^{21} , R^{22} , and R^{23} are independently hydrogen, haloalkyl, substituted or unsubstituted alkyl, substituted or unsubstituted cycloalkyl, substituted or unsubstituted aryl, substituted or unsubstituted heteroaryl, or substituted or unsubstituted cycloalkyl.

2. The compound of claim 1, wherein X^1 is $C(R^{15})$.
3. The compound of claim 1, wherein X^2 is $C(R^{15})$.
4. The compound of claim 1, wherein X^1 is $C(R^{15})$; and X^2 is $C(R^{15})$.
5. The compound of claim 1 or 3, wherein X^1 is N.
6. The compound of claim 1 or 2, wherein X^2 is N.
7. The compound of claim 1, 3, or 6, wherein X^1 is $(O^+)X^-$ or $(S^+)X^-$.
8. The compound of claim 1, 2, or 5, wherein X^2 is $(O^+)X^-$ or $(S^+)X^-$.
9. The compound of any one of claims 1-8, wherein R^{15} is hydrogen.
10. The compound of any one of claims 1-8, wherein R^{15} is substituted or unsubstituted alkyl.
11. The compound of any one of claims 1-8, wherein R^{15} is substituted or unsubstituted cycloalkyl.
12. The compound of any one of claims 1-8, wherein R^{15} is substituted or unsubstituted aryl.
13. The compound of any one of claims 1-8, wherein R^{15} is substituted or unsubstituted heteroaryl.
14. The compound of claim 1, wherein X^1 is N; and X^2 is N.
15. The compound of claim 1, wherein X^1 is $(O^+)X^-$ or $(S^+)X^-$; and X^2 is $(O^+)X^-$ or $(S^+)X^-$.
16. The compound of any one of claims 1-15, wherein at least one of $R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}$, and R^{14} is not hydrogen.
17. The compound of any one of claims 1-15, wherein at least two of $R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}$, and R^{14} are not hydrogen.
18. The compound of any one of claims 1-15, wherein at least three of $R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}$, and R^{14} are not hydrogen.
19. The compound of any one of claims 1-15, wherein at least four of $R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}$, and R^{14} are not hydrogen.
20. The compound of claim 1, wherein $R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}$, and

R^{14} are hydrogen; and X^1 is $C(R^{15})$, $(O^+)X^-$, or $(S^+)X^-$.

21. The compound of claim 1, wherein $R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}$, and R^{14} are hydrogen; X^1 is $C(R^{15})$, $(O^+)X^-$, or $(S^+)X^-$; and X^2 is $C(R^{15})$, $(O^+)X^-$, or $(S^+)X^-$.

22. The compound of claim 1, wherein $R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}$, and R^{14} are hydrogen; and X^1 is $C(R^{15})$.

23. The compound of claim 1, wherein $R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}$, and R^{14} are hydrogen; X^1 is $C(R^{15})$; and X^2 is $C(R^{15})$.

24. The compound of claim 1, wherein $R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}$, and R^{14} are hydrogen; and X^1 is $(O^+)X^-$ or $(S^+)X^-$.

25. The compound of claim 1, wherein $R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}$, and R^{14} are hydrogen; X^1 is $(O^+)X^-$ or $(S^+)X^-$; and X^2 is $(O^+)X^-$ or $(S^+)X^-$.

26. The compound of claim 1, wherein $R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}$, and R^{14} are hydrogen; X^1 is N; and X^2 is N.

27. The compound of claim 1, wherein X^1 is N; and the compound of Formula I is a Bronsted conjugate acid or a quaternary (C₁-C₆)alkyl ammonium salt at X^1 .

28. The compound of claim 1, wherein X^2 is N; and the compound of Formula I is a Bronsted conjugate acid or a quaternary (C₁-C₆)alkyl ammonium salt at X^2 .

29. The compound of claim 1, wherein X^1 is N; X^2 is N; the compound of Formula I is a Bronsted conjugate acid or a quaternary (C₁-C₆)alkyl ammonium salt at X^1 ; and the compound of Formula I is a Bronsted conjugate acid or a quaternary (C₁-C₆)alkyl ammonium salt at X^2 .

30. A composition, comprising a compound of any one of claims 1-29; and a support material; wherein the compound is in contact with the support material.

31. The composition of claim 30, wherein the support material comprises carbon.

32. The composition of claim 30, wherein the support material comprises carbon powder.

33. The composition of claim 30, wherein the support material comprises carbon black (CB), multi-walled carbon nanotubes (MWCNT), graphene oxide (GO), or reduced graphene oxide (rGO).

34. The composition of any one of claims 30-33, wherein the compound is adsorbed on the support material.
35. A cathode catalyst, comprising a compound of any one of claims 1-29 or a composition of any one of claims 27-31.
36. A fuel cell, comprising a cathode catalyst of claim 35.
37. A method of reducing oxygen, comprising:
in an electrochemical device, applying current to a mixture comprising an aqueous medium, hydrogen gas, oxygen gas, and a compound of any one of claims 1-26 or a composition of any one of claims 30-34.
38. The method of claim 36, wherein the aqueous medium is an alkaline medium.
39. The method of claim 37, wherein the electrochemical device is an anion-exchange membrane fuel cell or an alkaline metal-air battery.
40. The method of claim 36, wherein the aqueous medium is an acidic medium.
41. The method of claim 39, wherein the electrochemical device is a proton-exchange membrane fuel cell.

FIG. 1

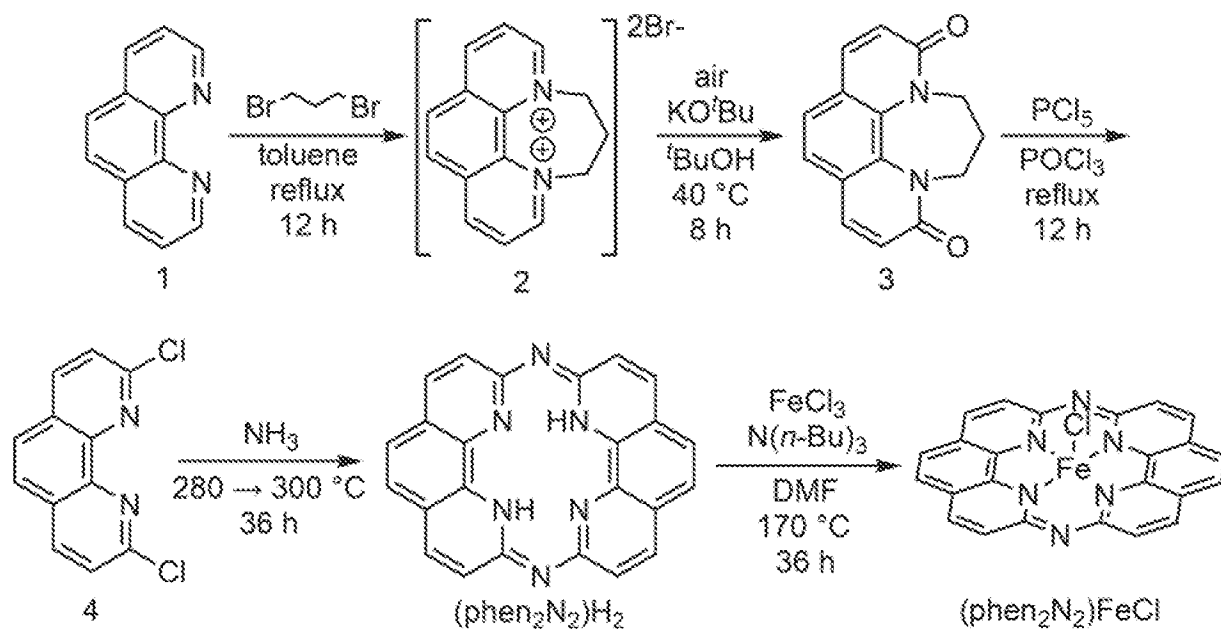


FIG. 2

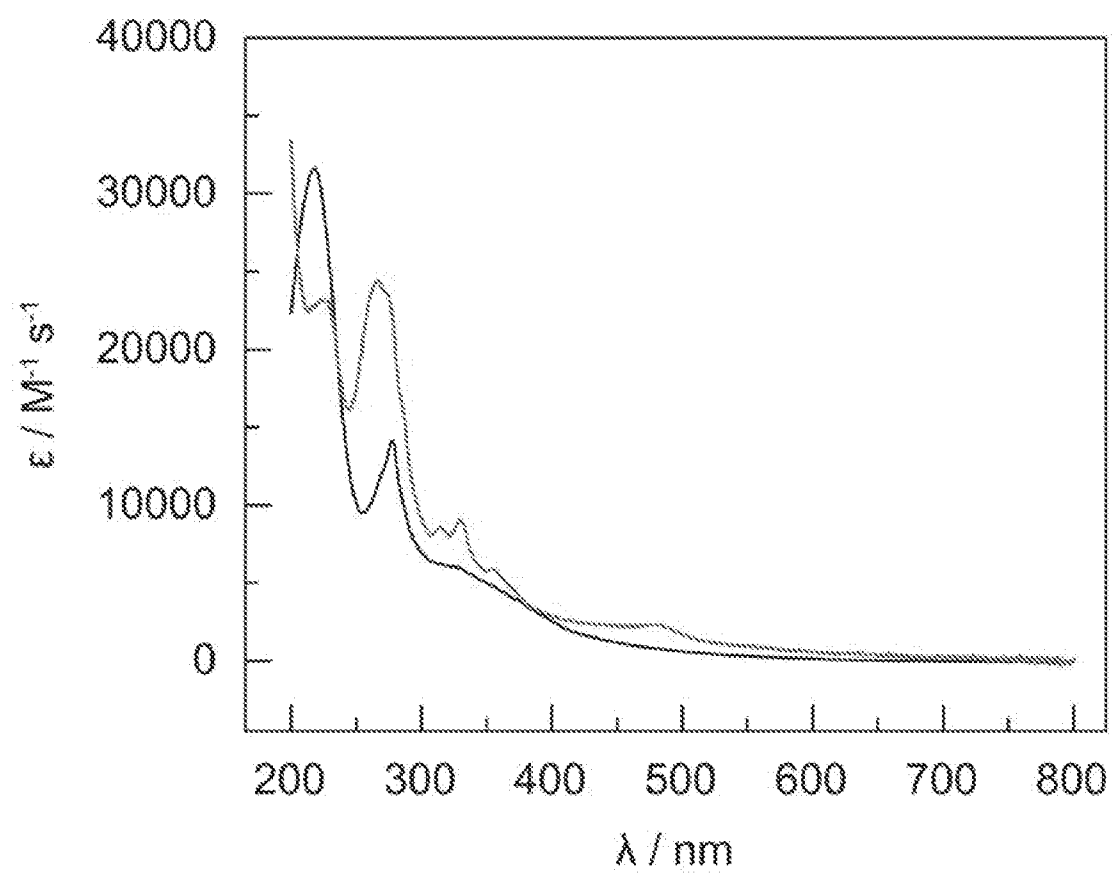


FIG. 3

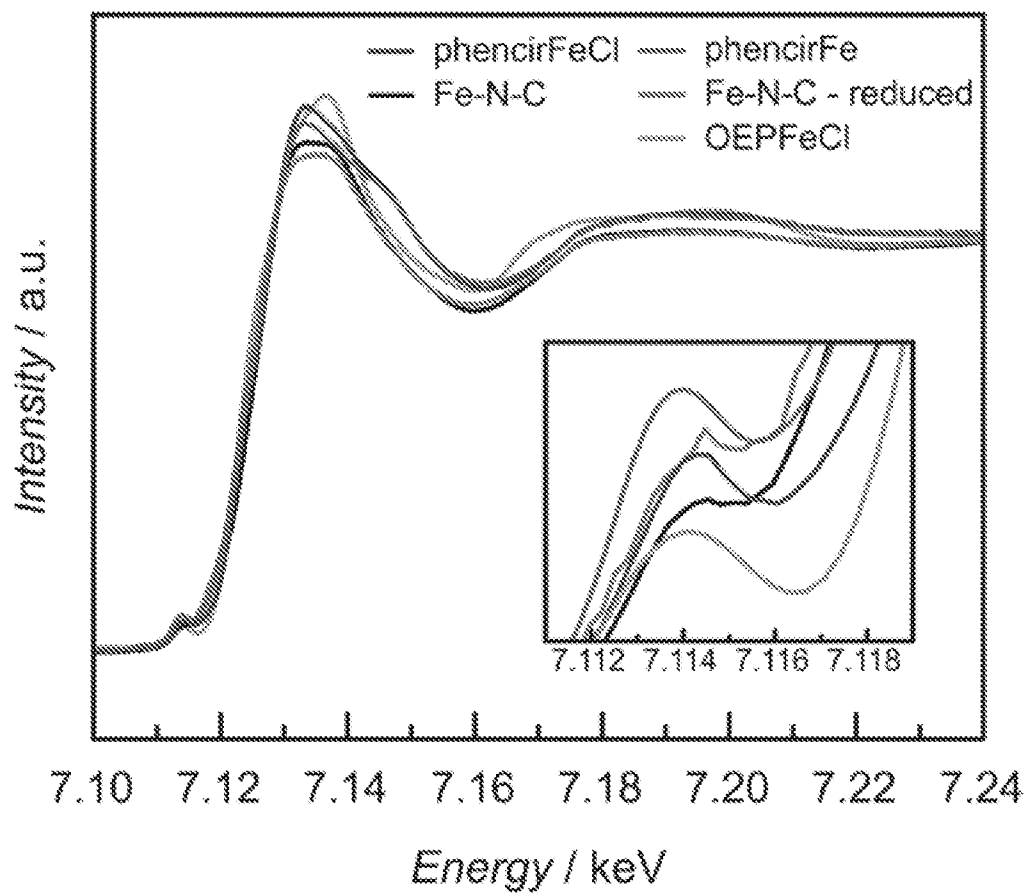


FIG. 4

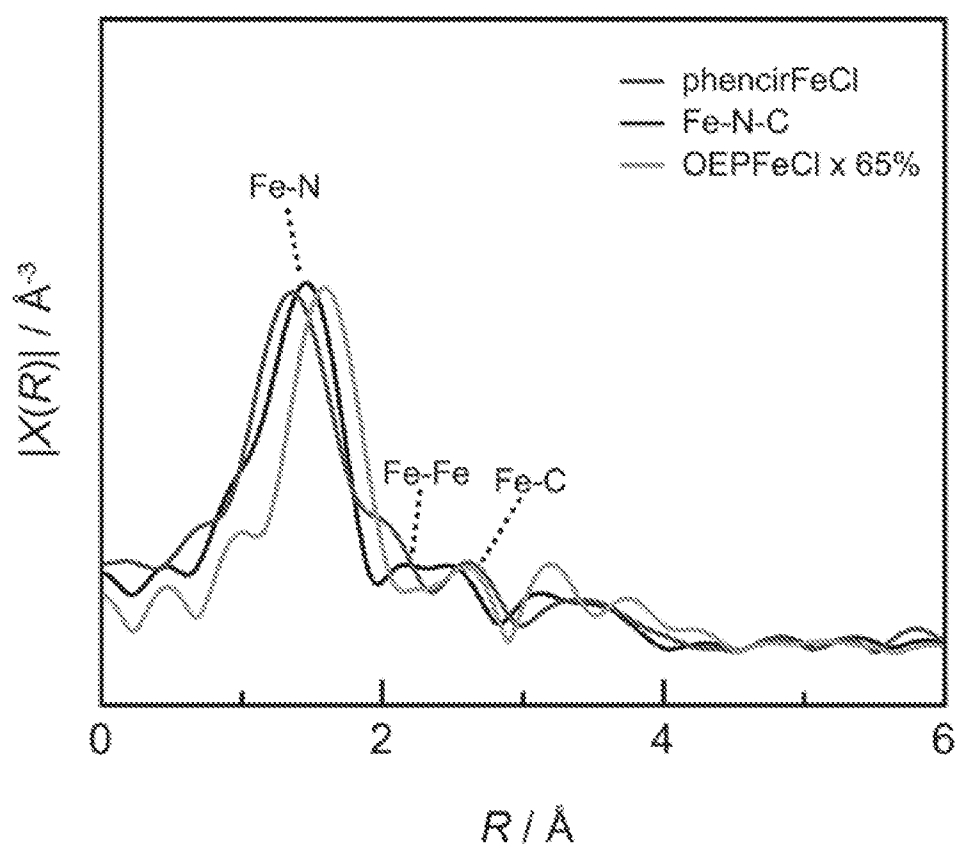
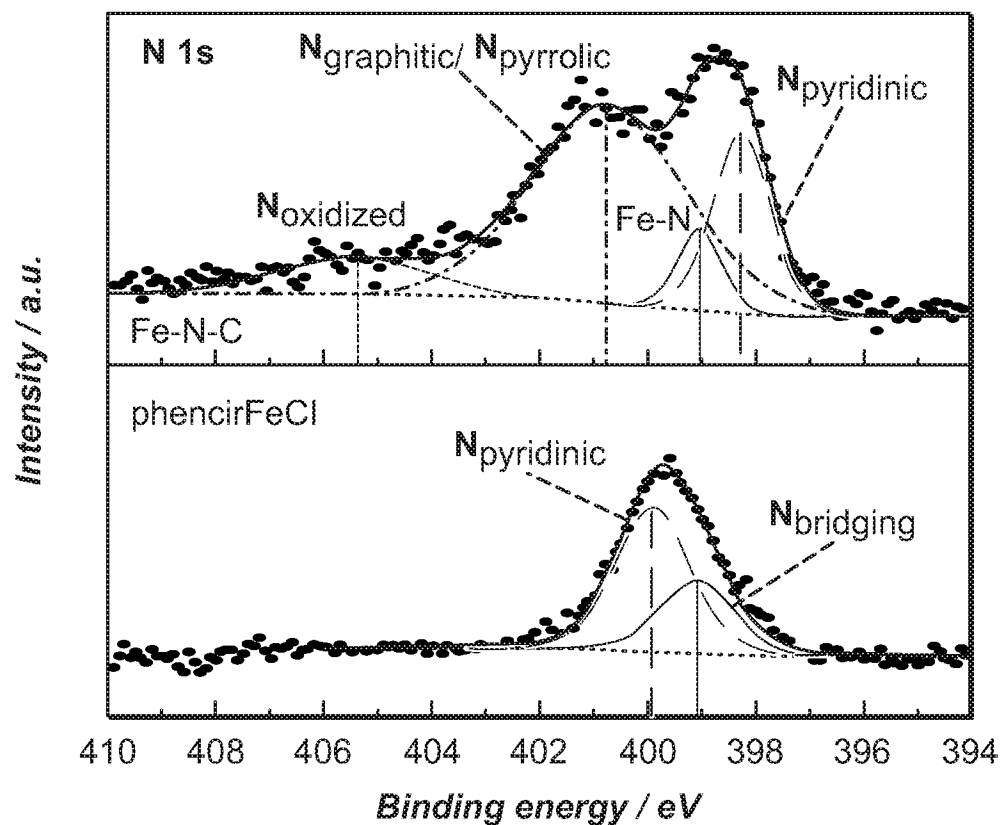


FIG. 5

A



B

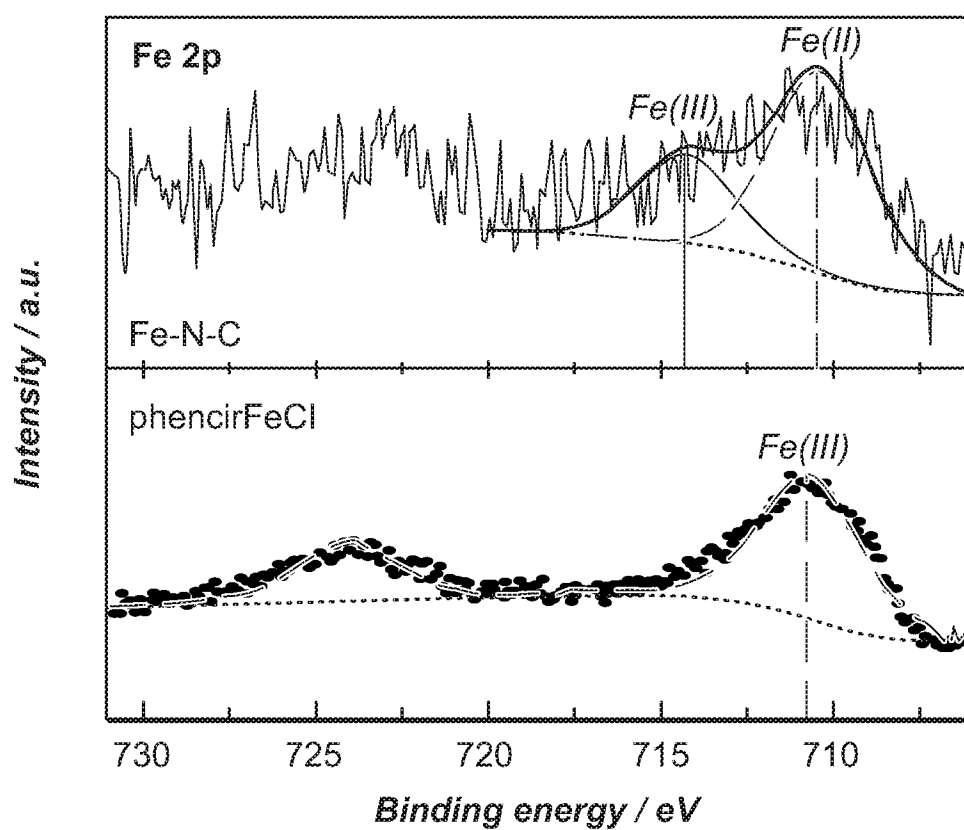
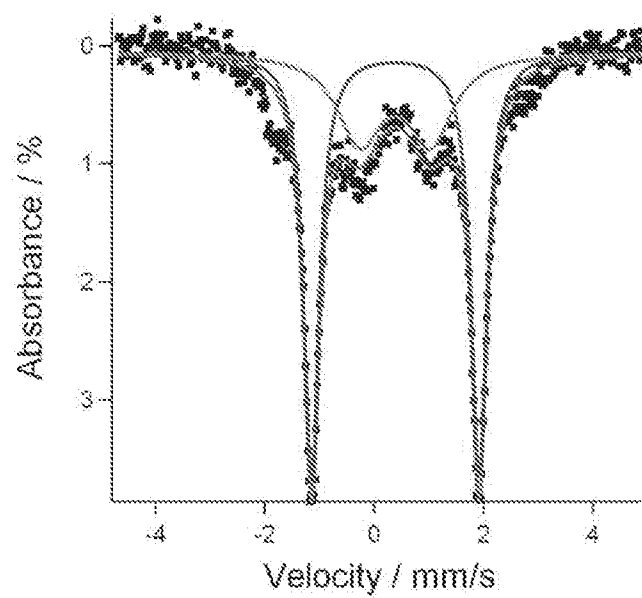


FIG. 6

A



B

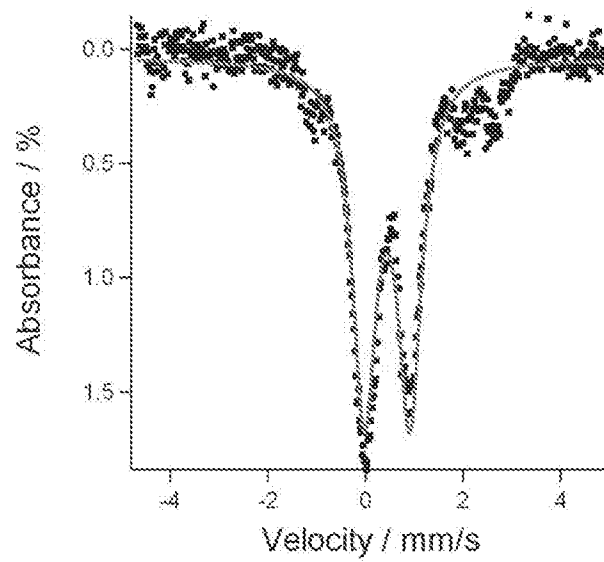


FIG. 7

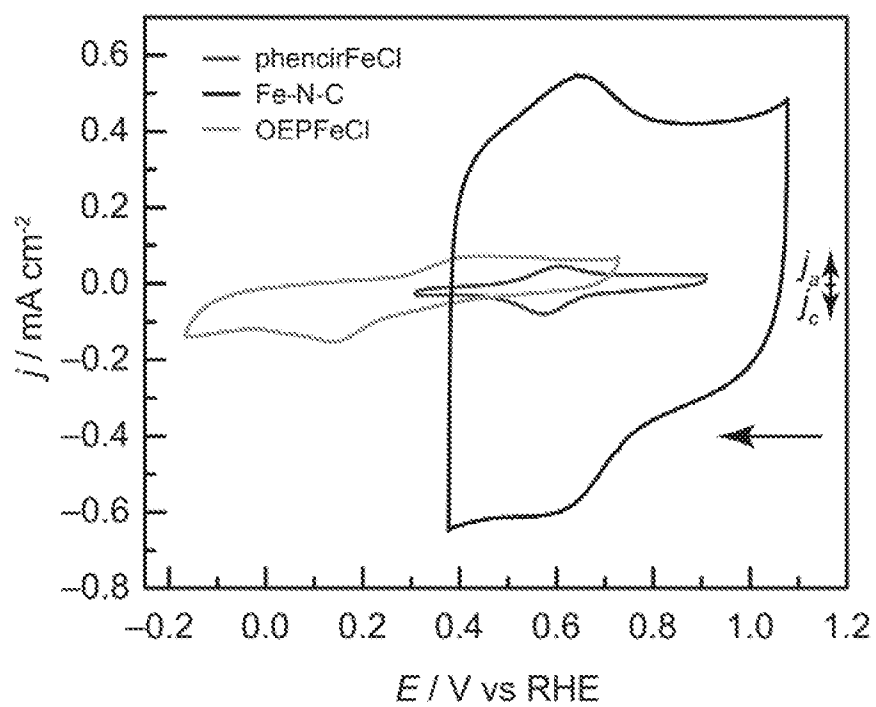


FIG. 8

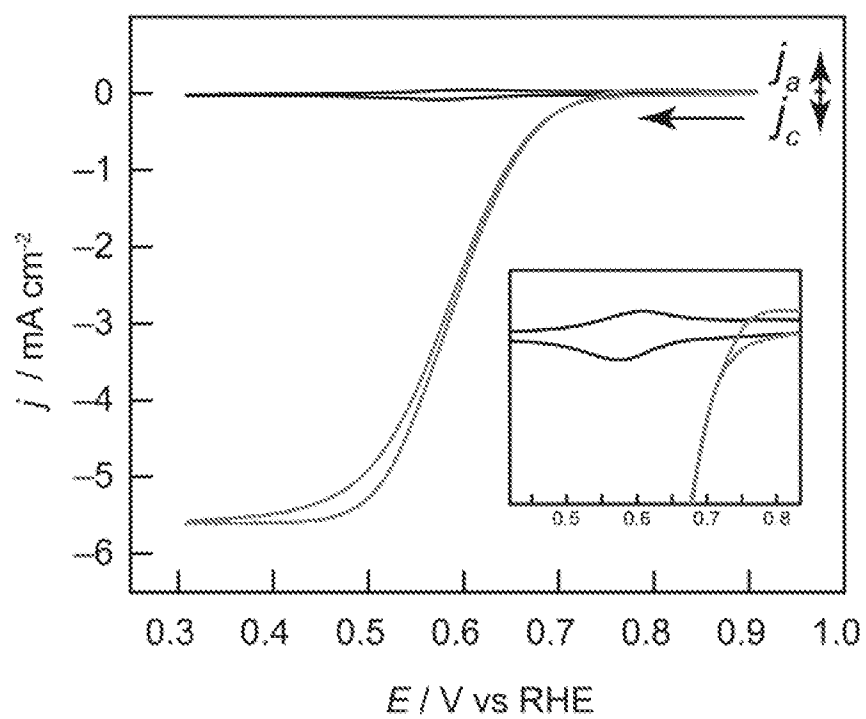


FIG. 9

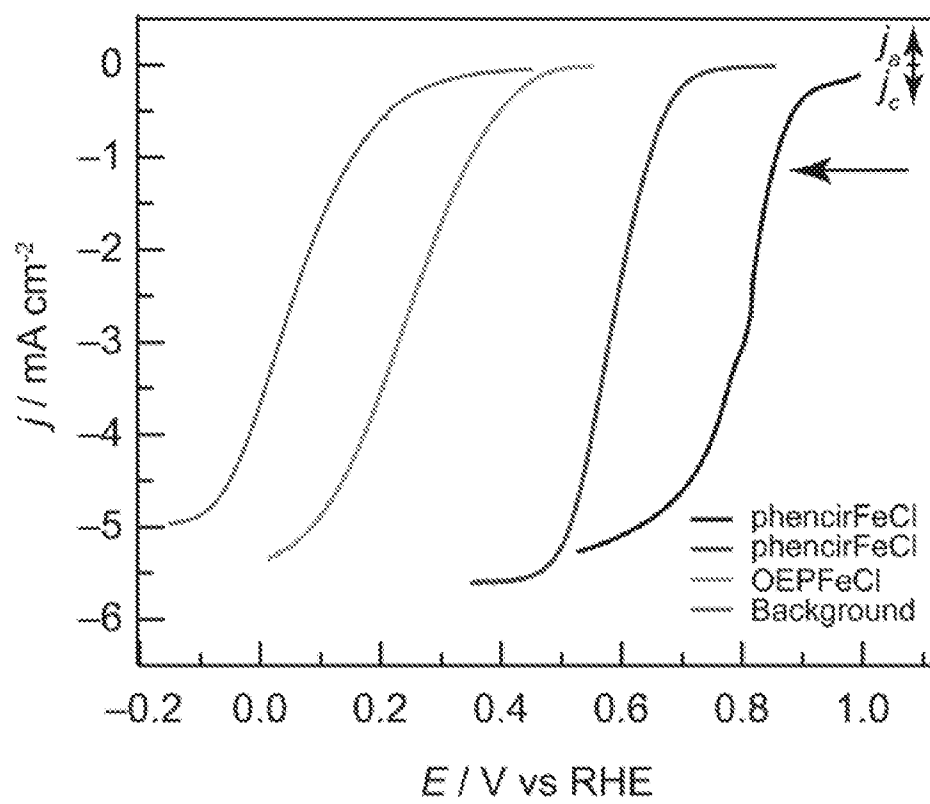


FIG. 10

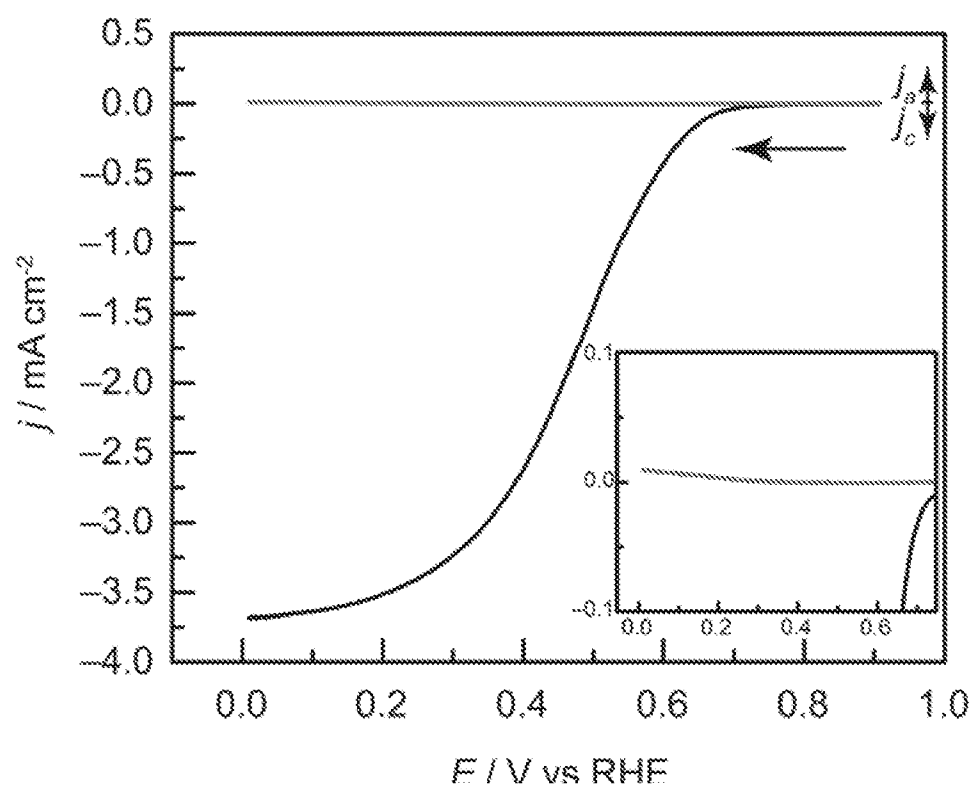
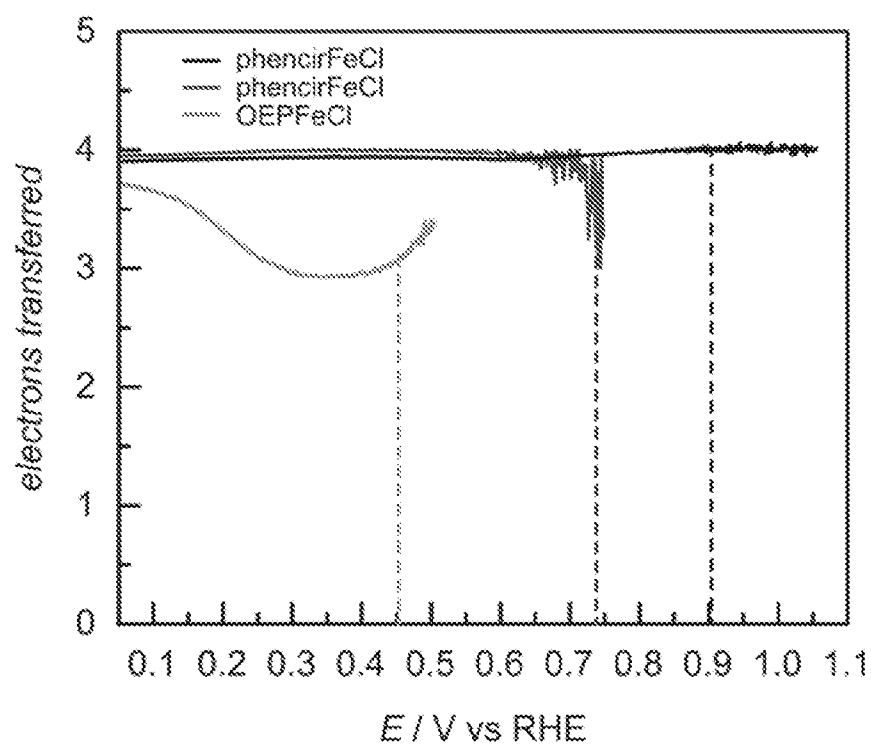


FIG. 11



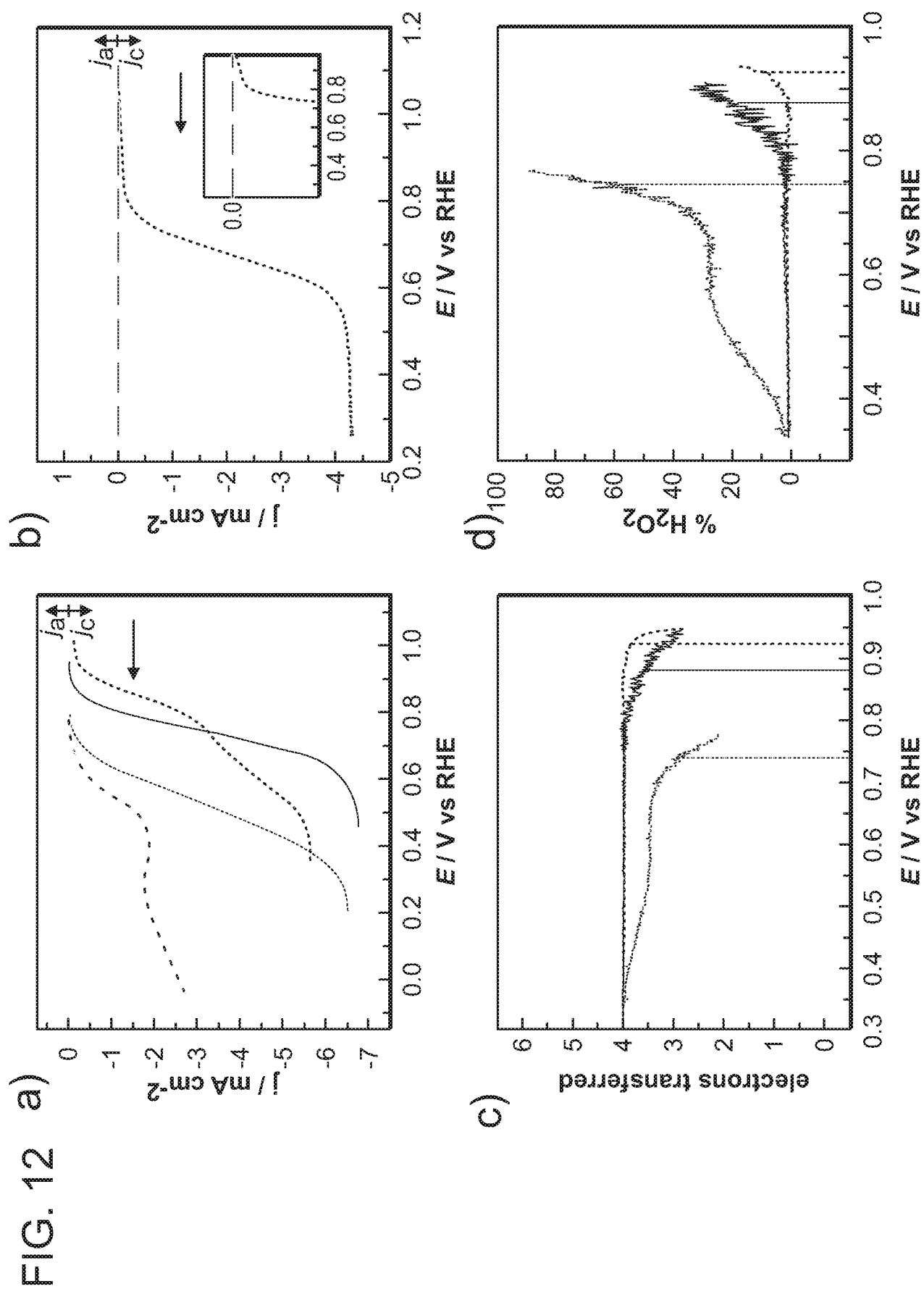


FIG. 13

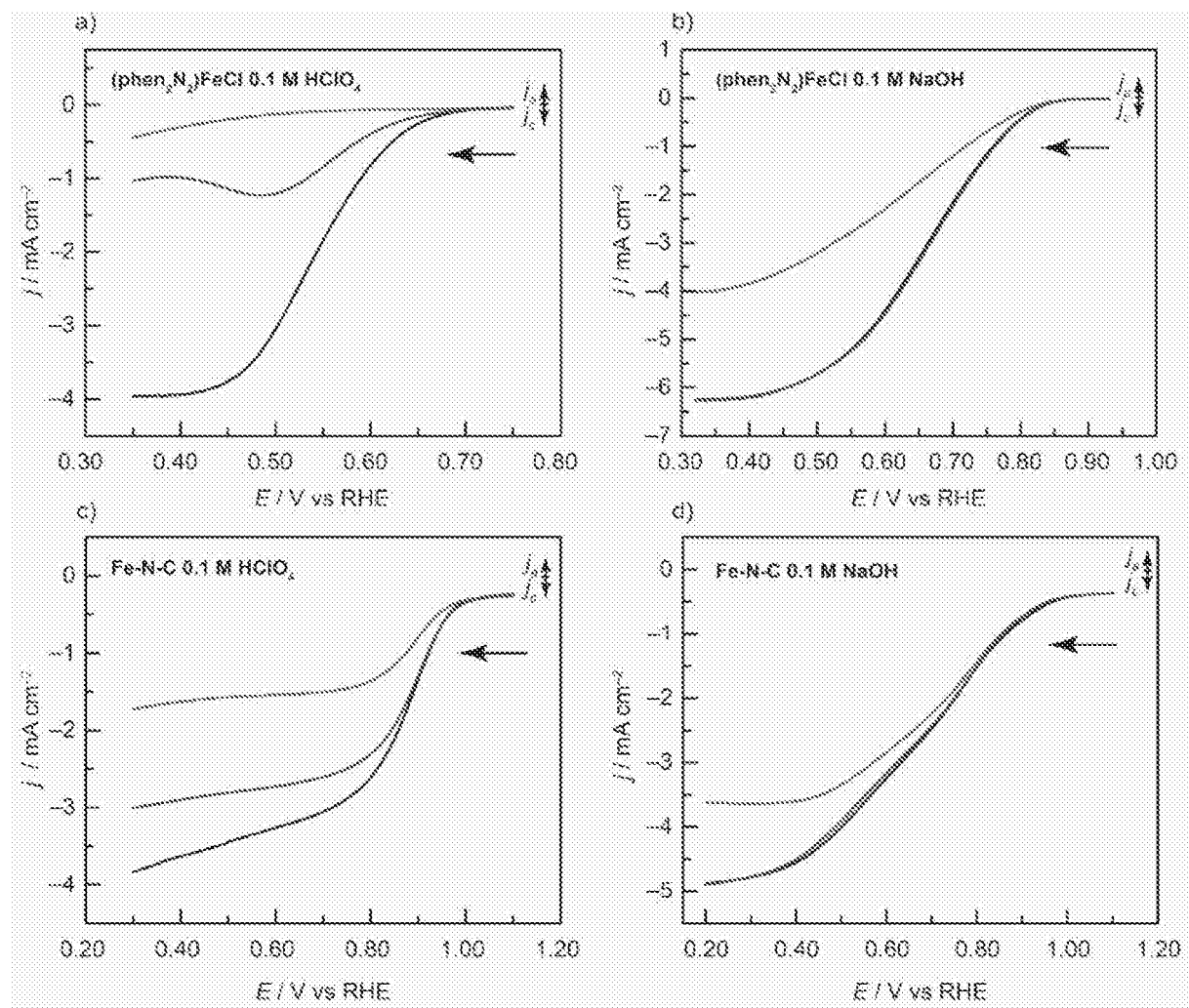


FIG. 14

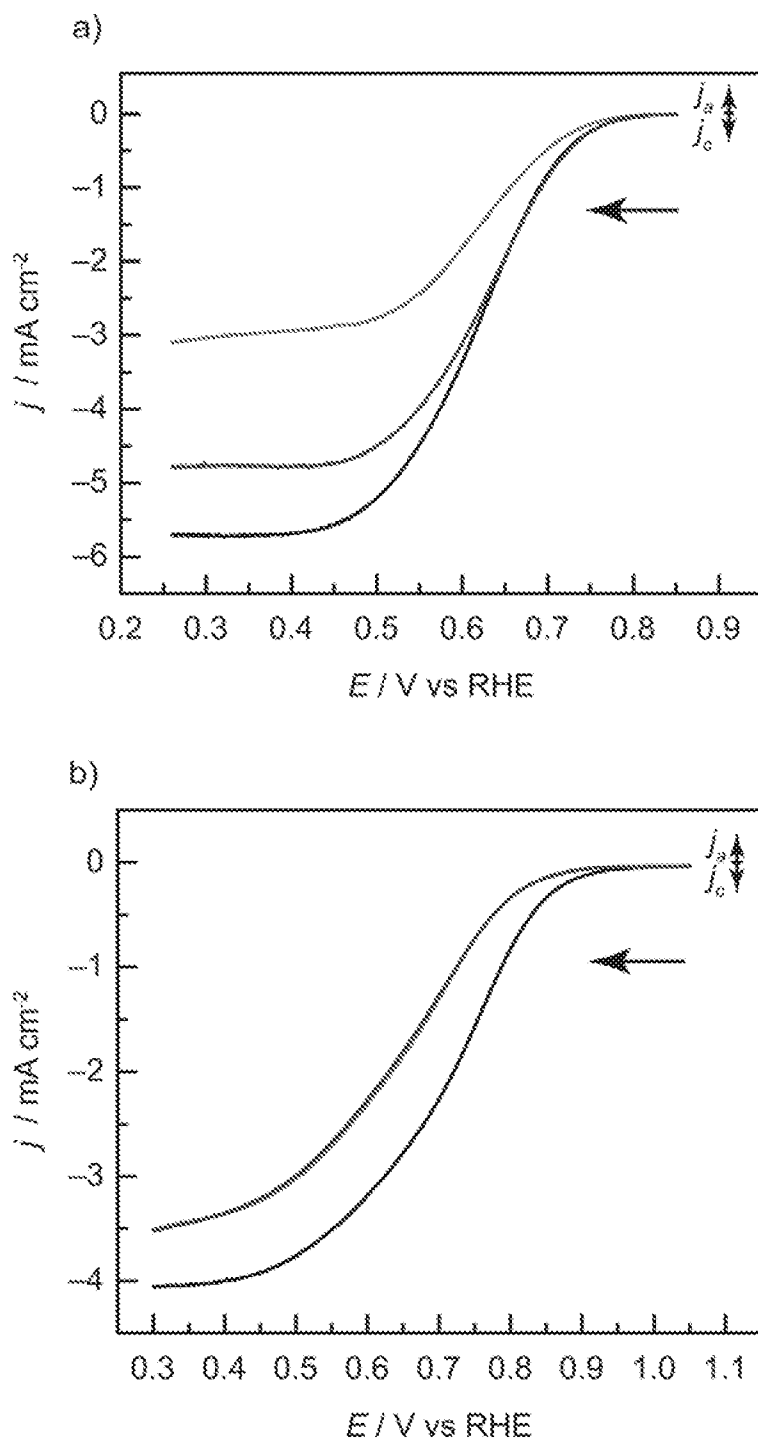
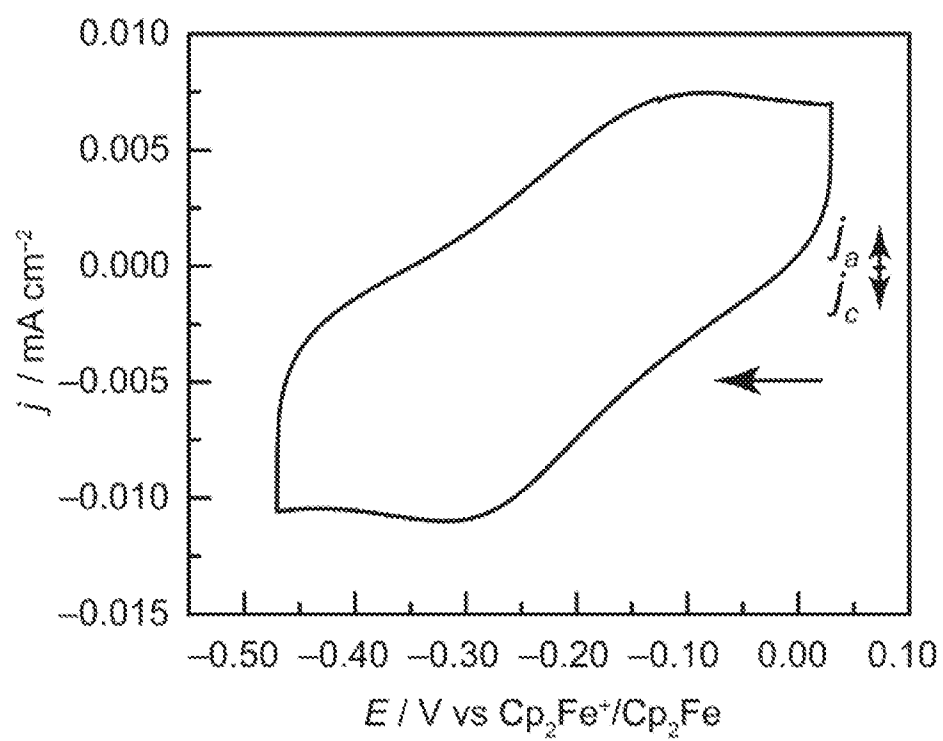


FIG. 15



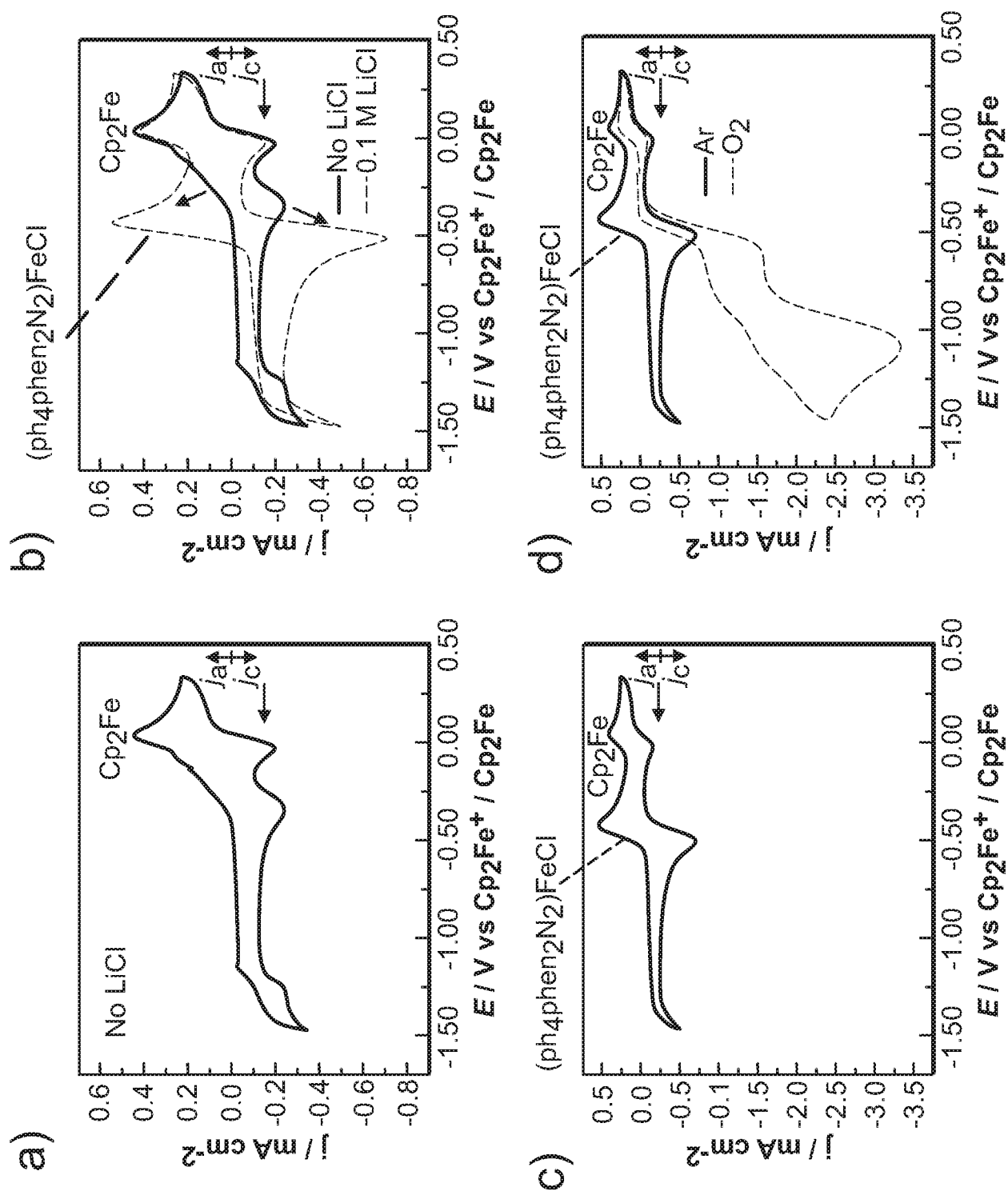


FIG. 17

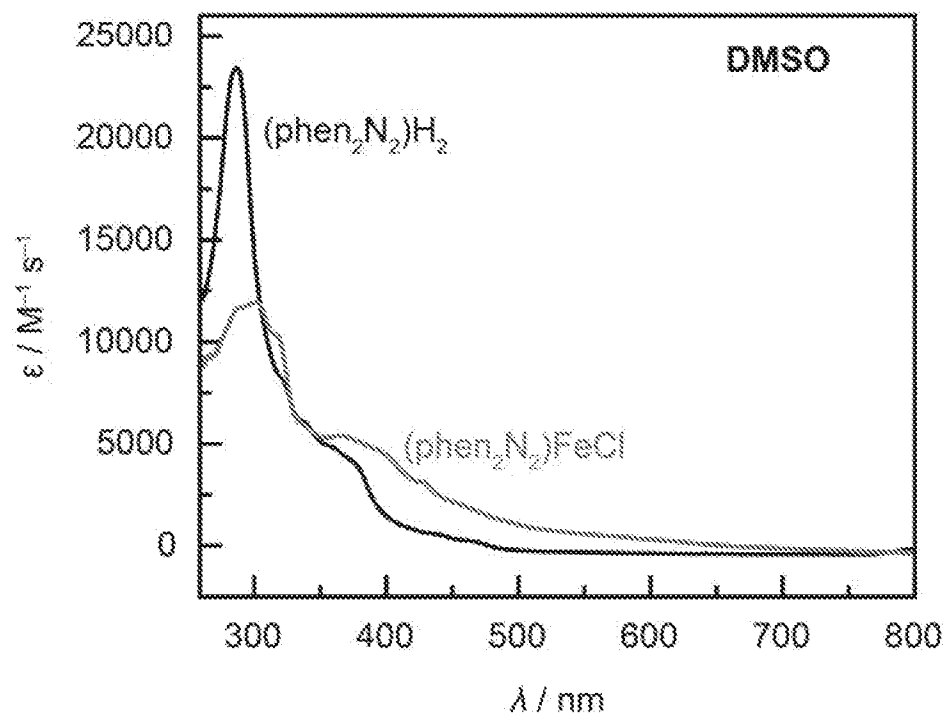
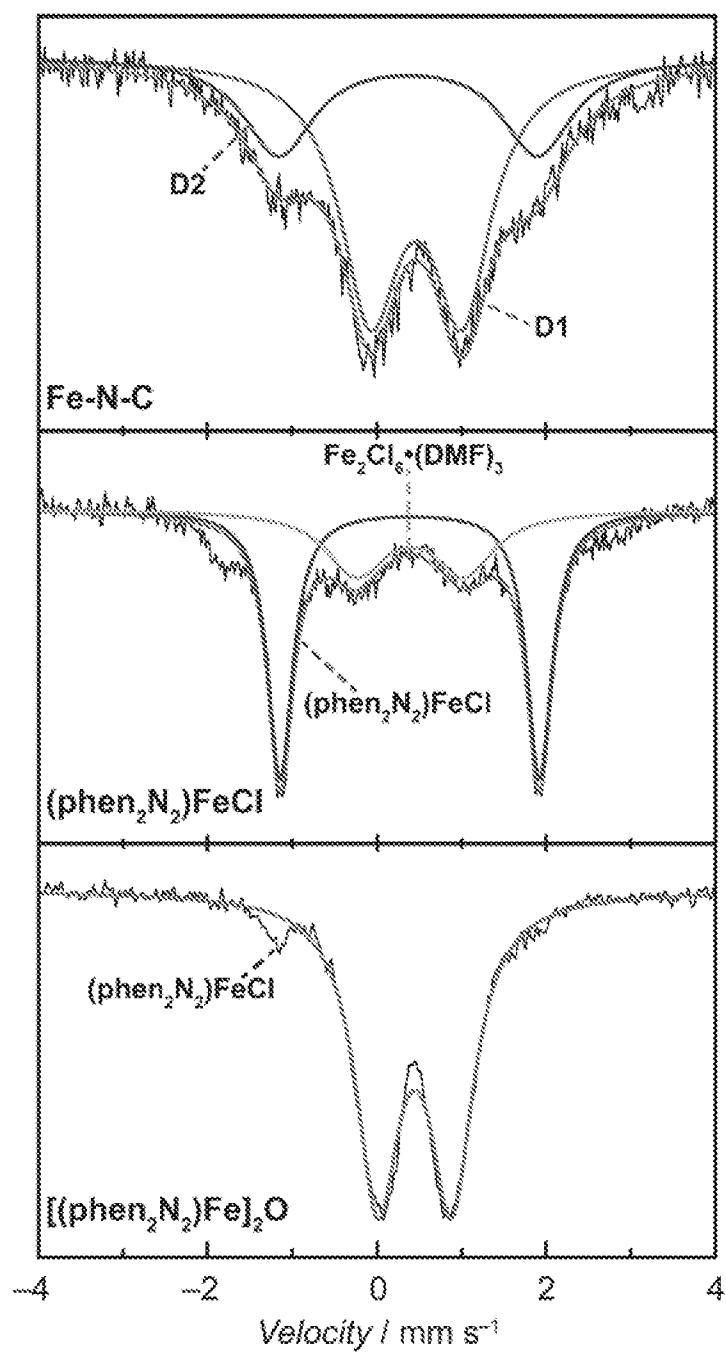


FIG. 18



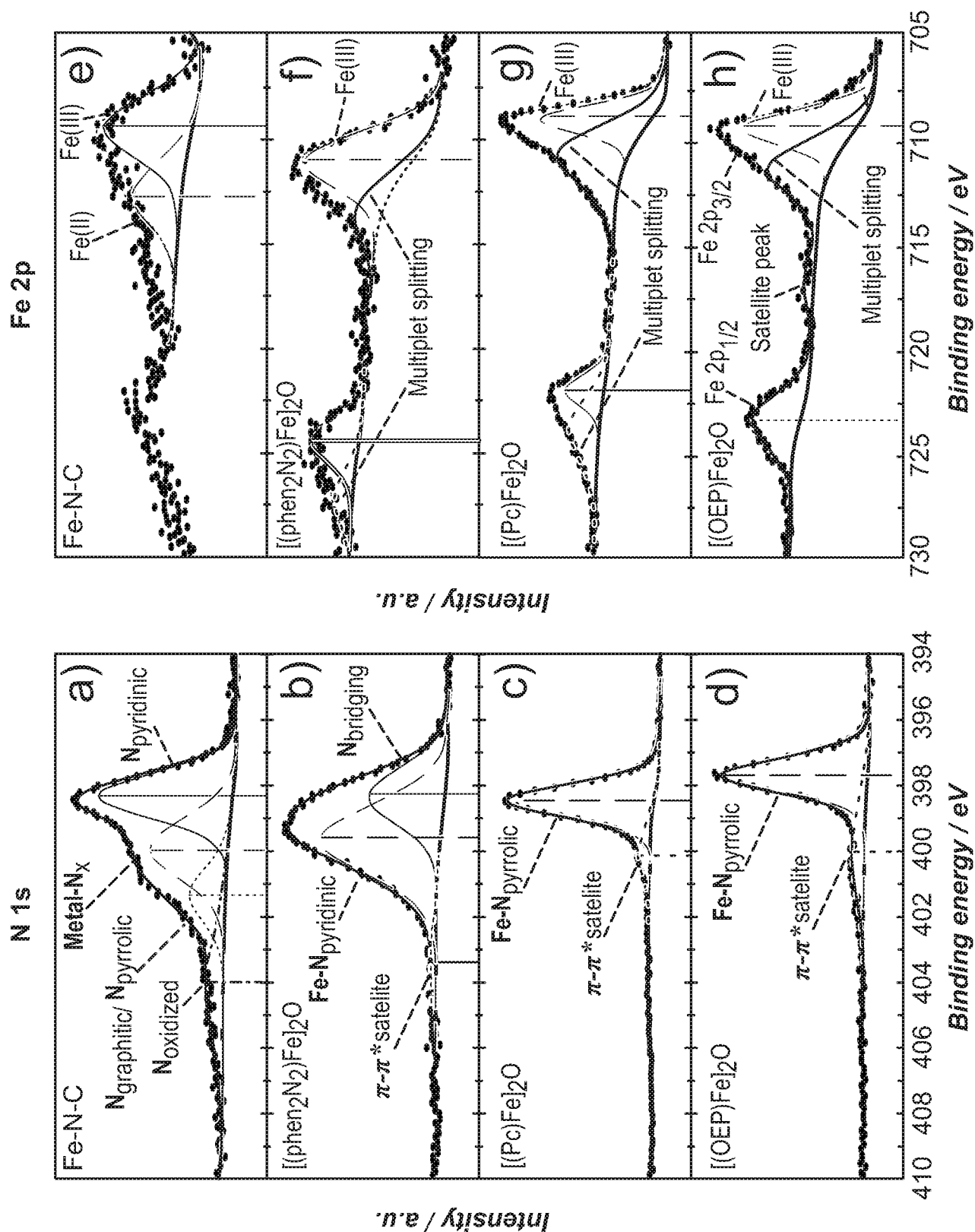


FIG. 20

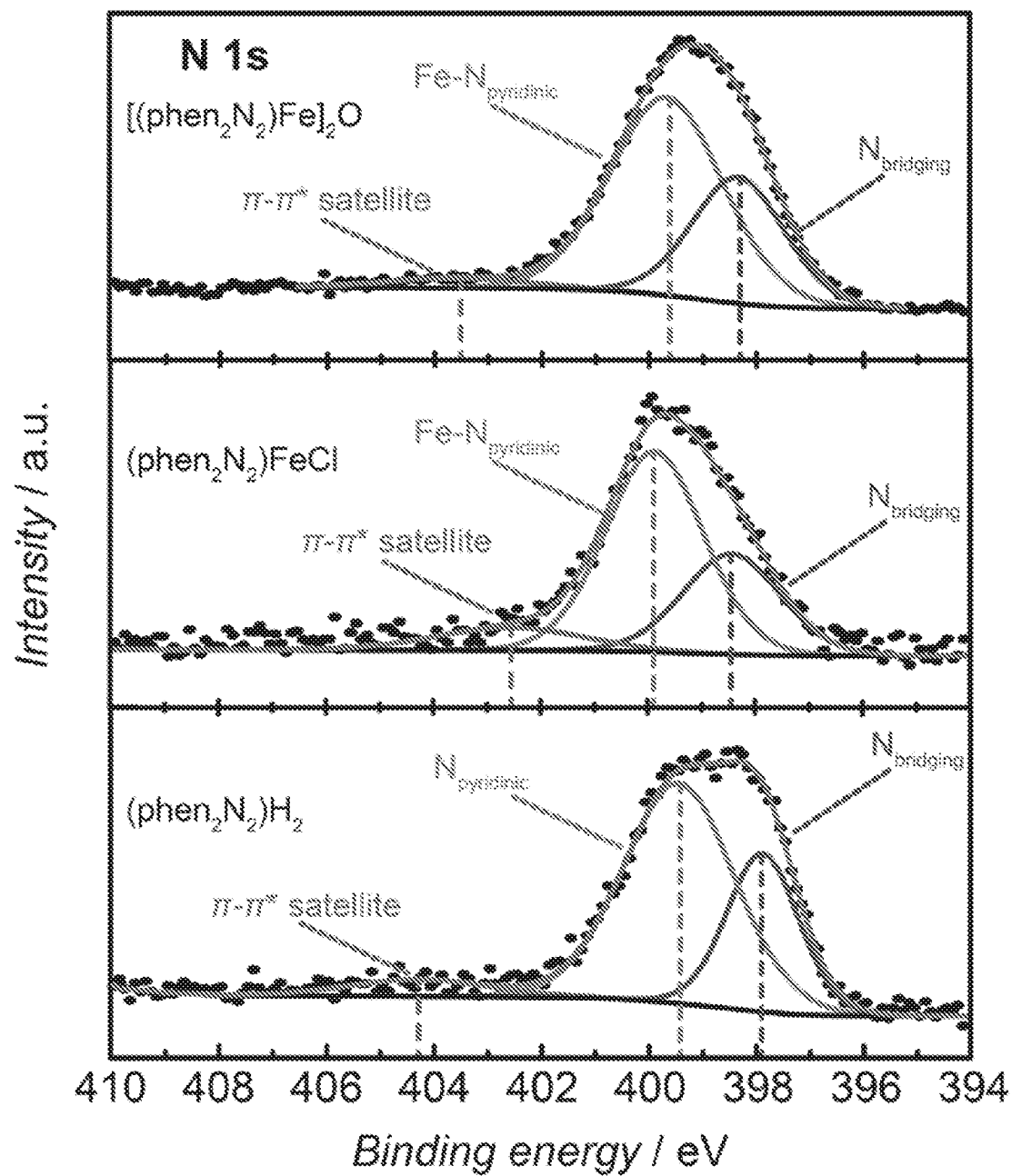
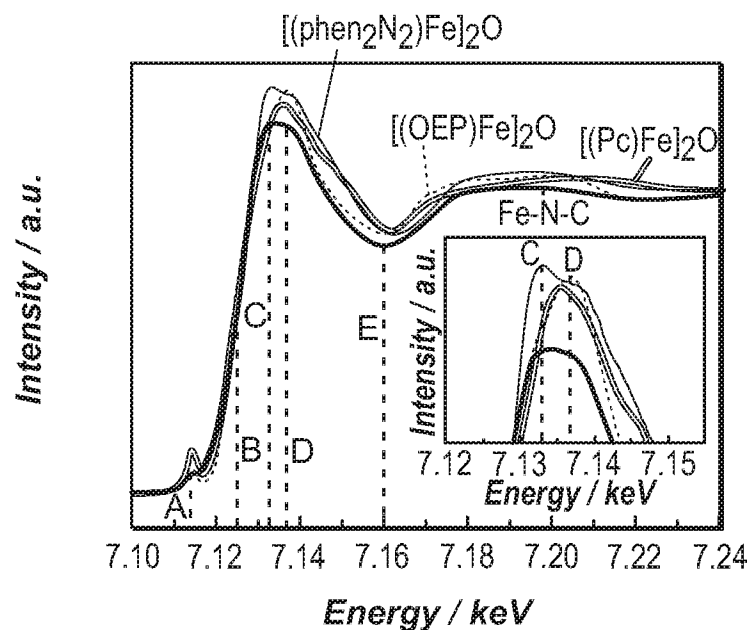
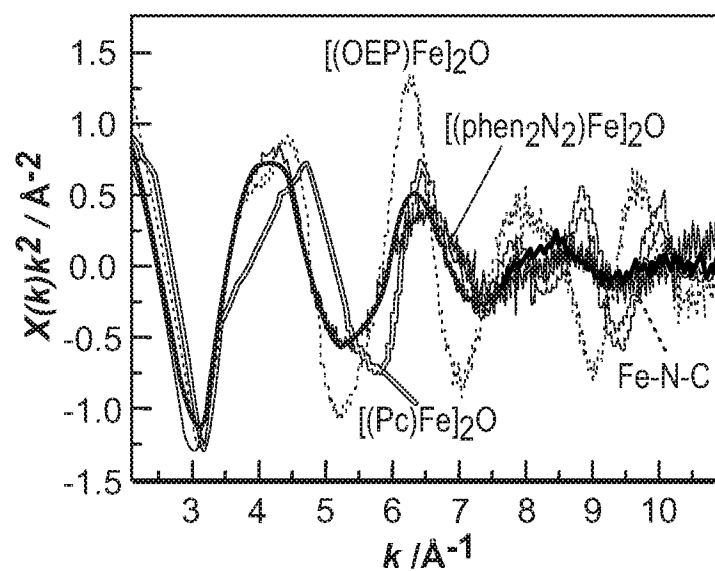


FIG. 21

a)



b)



c)

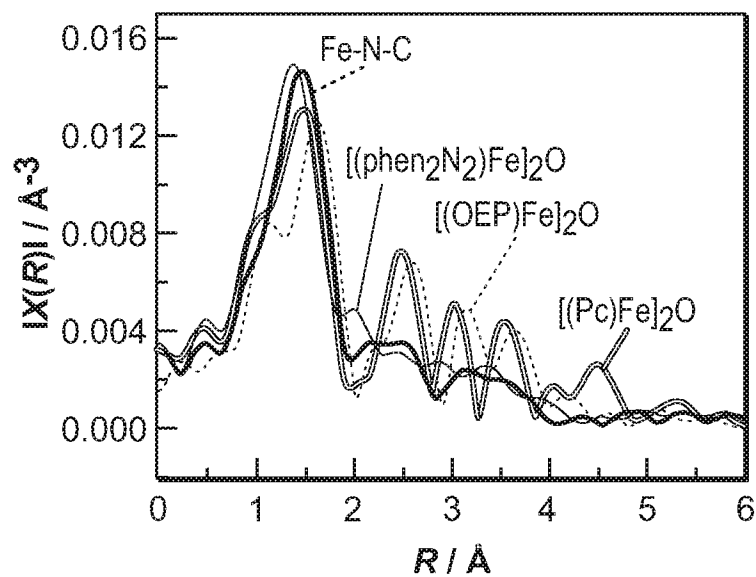


FIG. 22

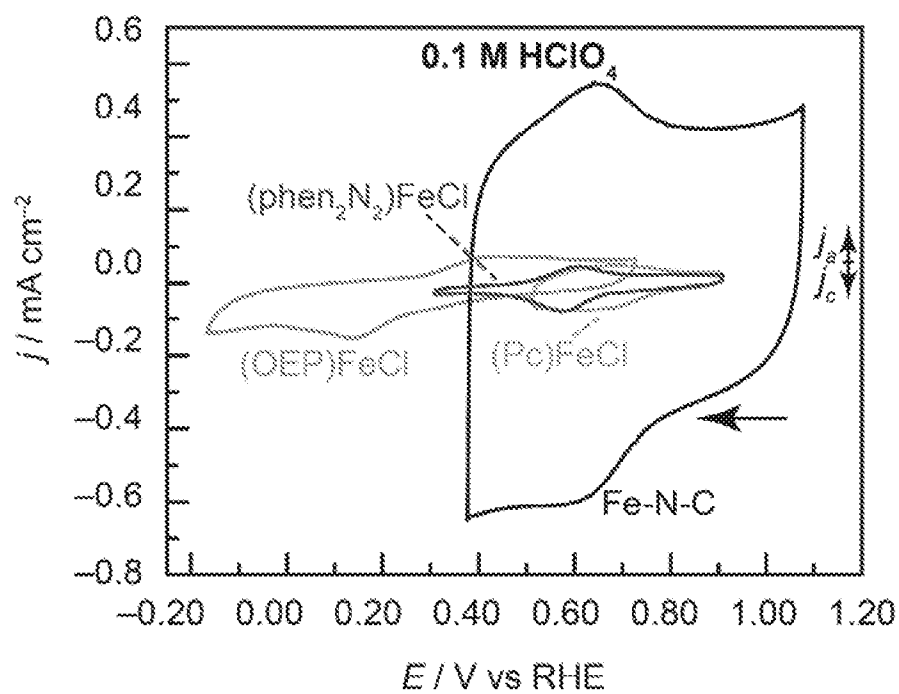


FIG. 23

Catalyst Ink	Catalyst Mass ^a / mg cm ⁻²	Total Mass / mg cm ⁻²	Moles catalyst / 1 x 10 ⁻⁷ mol cm ⁻²	Electroactive Moles ^b / 1 x 10 ⁻⁷ mol cm ⁻²
(phen ₂ N ₂)FeCl ^c	0.056	0.18	1.2	0.085
(OEP)FeCl ^c	0.056	0.18	0.90	0.39
(Pc)FeCl ^d	0.077	0.27	1.3	0.14
Fe-N-C ^e	0.24	0.24	—	—
(phen ₂ N ₂)H ₂ ^f	0.046	0.21	1.2	—
Vulcan ^g	0	0.51	—	—

FIG. 24

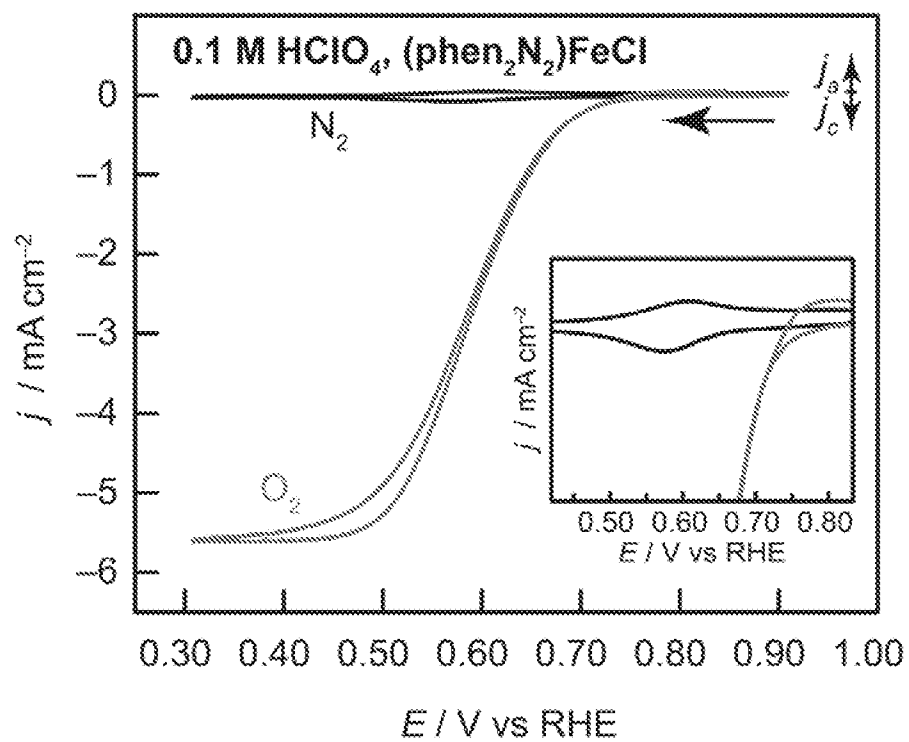


FIG. 25

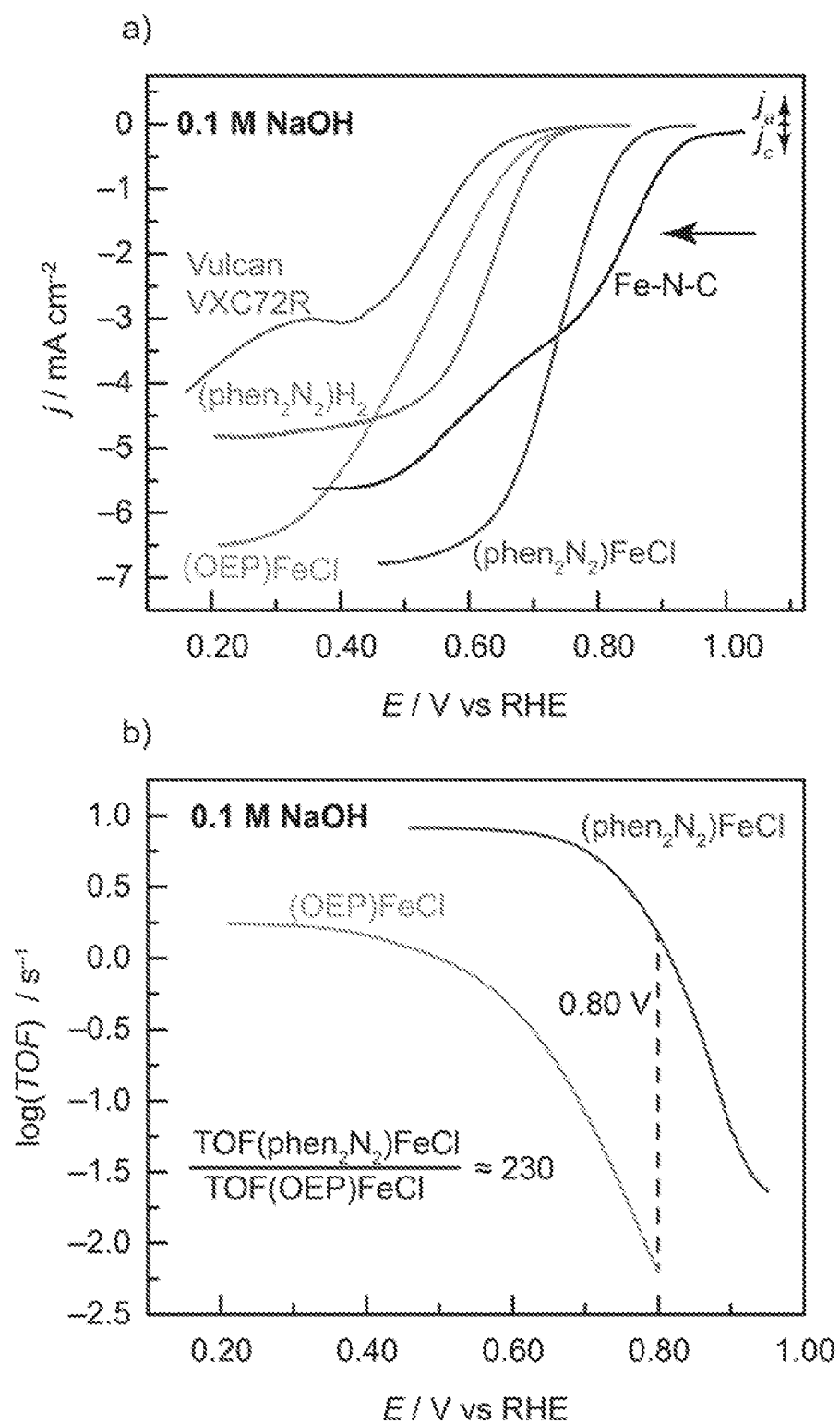


FIG. 26

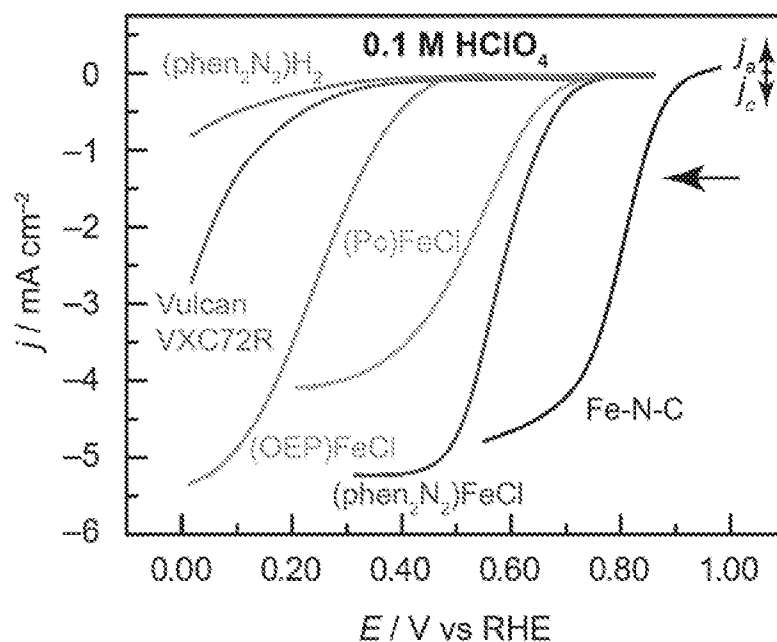


FIG. 27

Material/Complex (Carbon support)	Electrolyte	$E_{1/2}$ / V ^a	Onset / V ^b	Max %H ₂ O ₂	Total Metal Loading / $\mu\text{g cm}^{-2}$
(phen ₂ N ₂)FeCl (Vulcan)	0.1 M HClO ₄	0.59	0.75	2	6.6
	0.1 M NaOH	—	0.88	3	
(OEP)FeCl (Vulcan)	0.1 M HClO ₄	0.27	0.45	29	5.0
	0.1 M NaOH	—	0.74	5	
(Pc)FeCl (Vulcan)	0.1 M HClO ₄	0.61	0.75	9	7.1
	0.1 M NaOH	—	0.89	11	
Fe-N-C	0.1 M HClO ₄	—	0.90	3	2.6
	0.1 M NaOH	—	0.94	9	
(phen ₂ N ₂)H ₂ (Vulcan)	0.1 M NaOH	—	0.75	26	—

FIG. 28

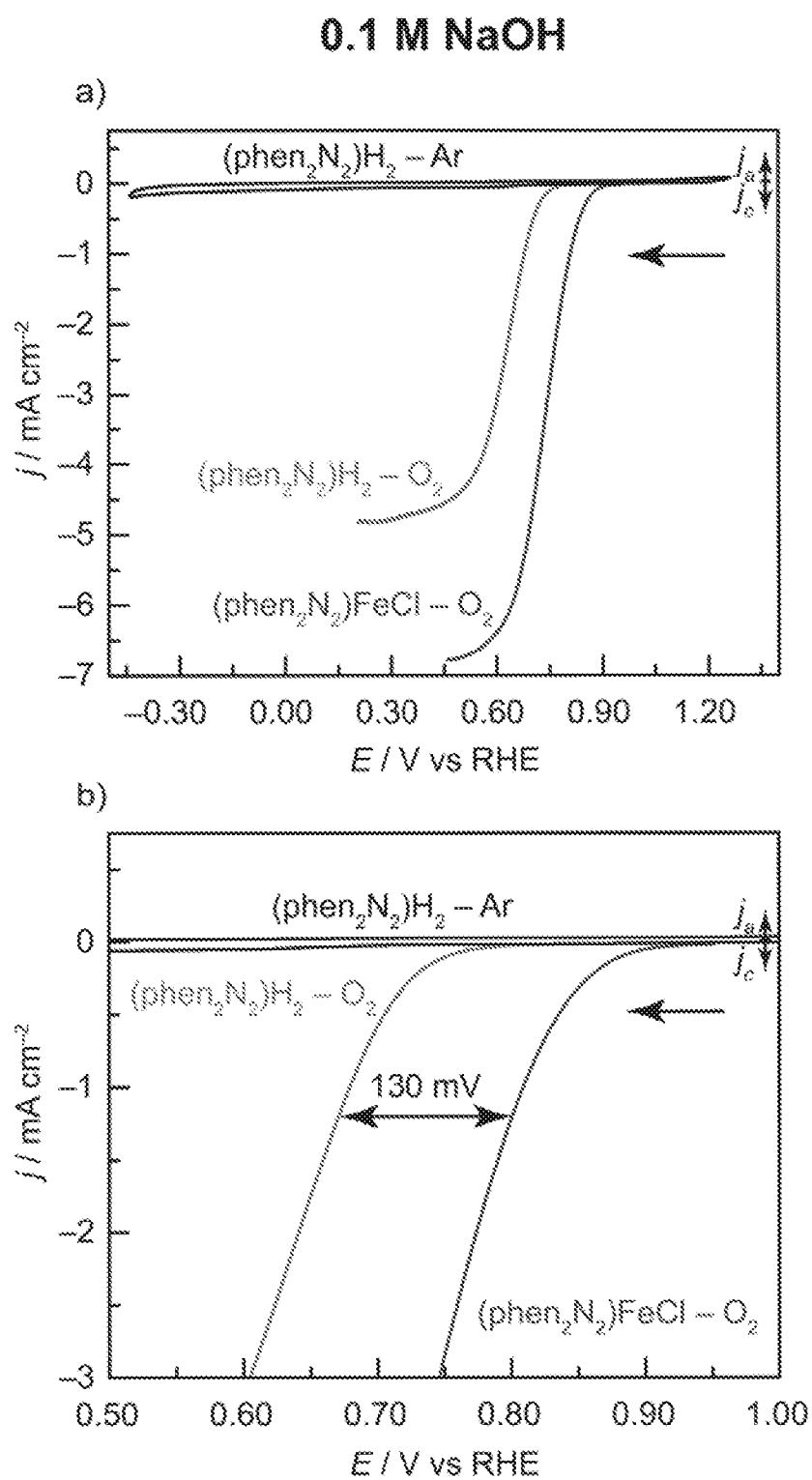


FIG. 29

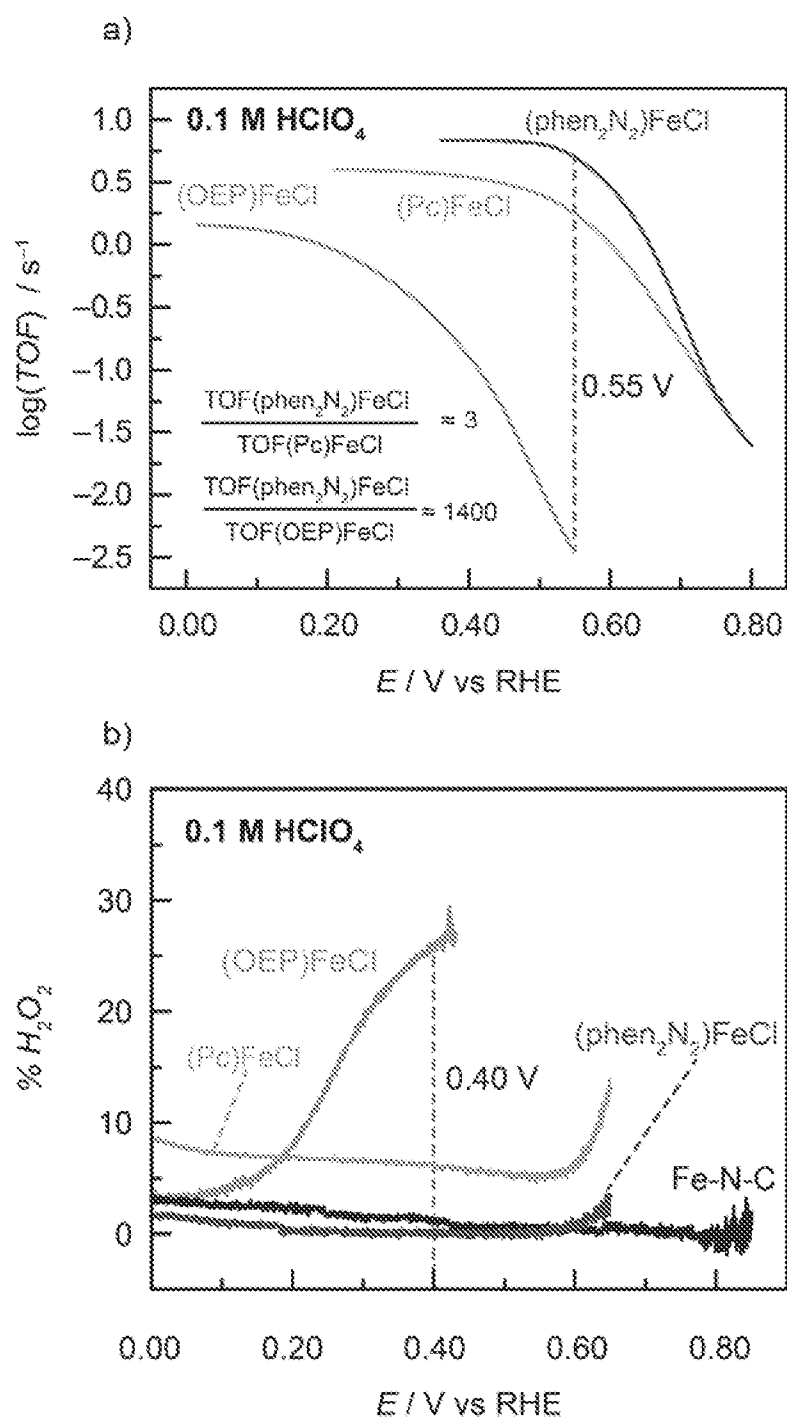


FIG. 30

Catalyst	Electroactive Moles / $1 \times 10^{-7} \text{ mol cm}^{-2}$	TOF in 0.1 M HClO ₄ @ 0.55 V vs RHE / s ⁻¹	TOF in 0.1 M NaOH @ 0.80 V vs RHE / s ⁻¹
(phen ₂ N ₂)FeCl	0.085	5.0	1.5
(OEP)FeCl	0.39	0.0035	0.0062

FIG. 31

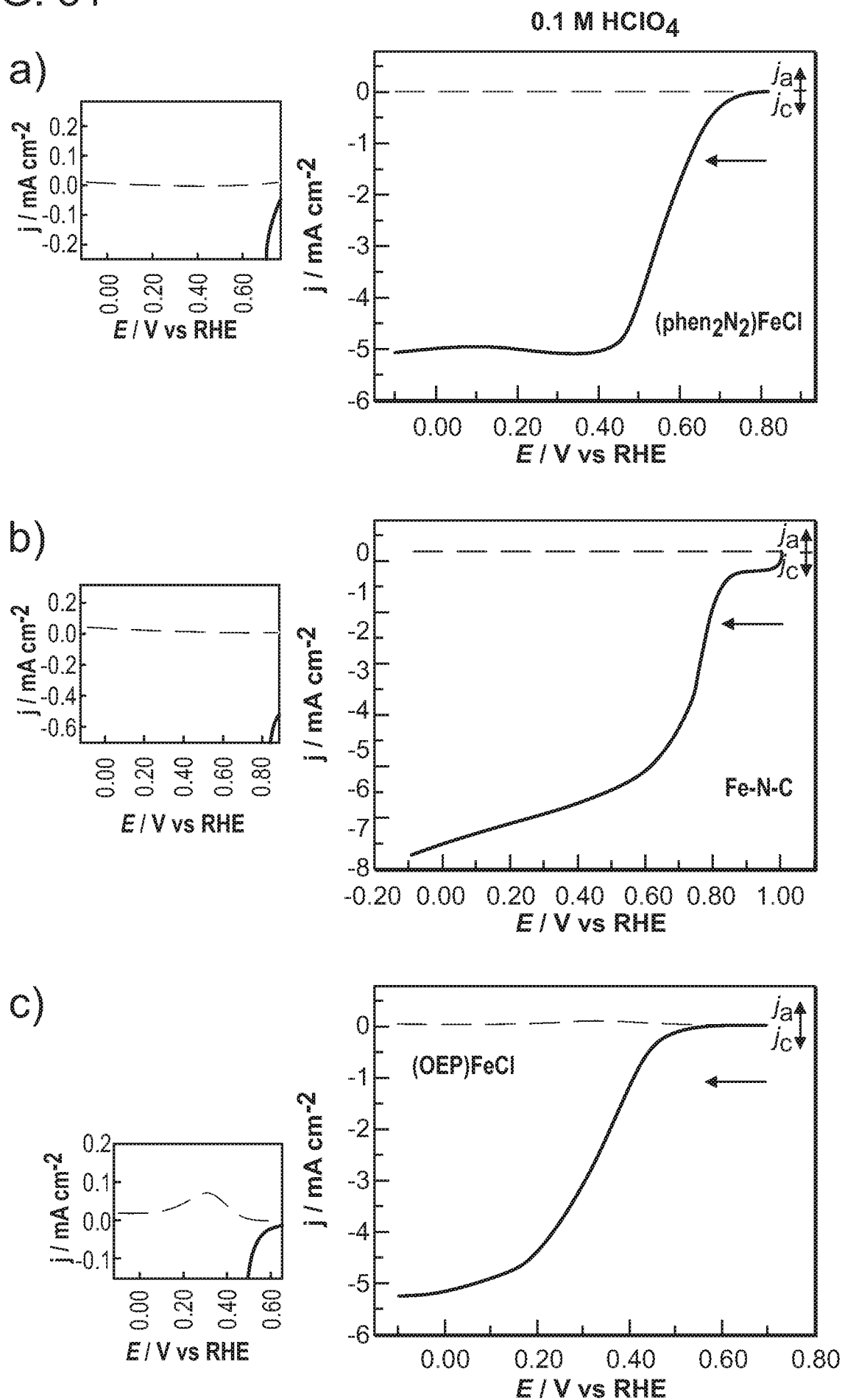


FIG. 32

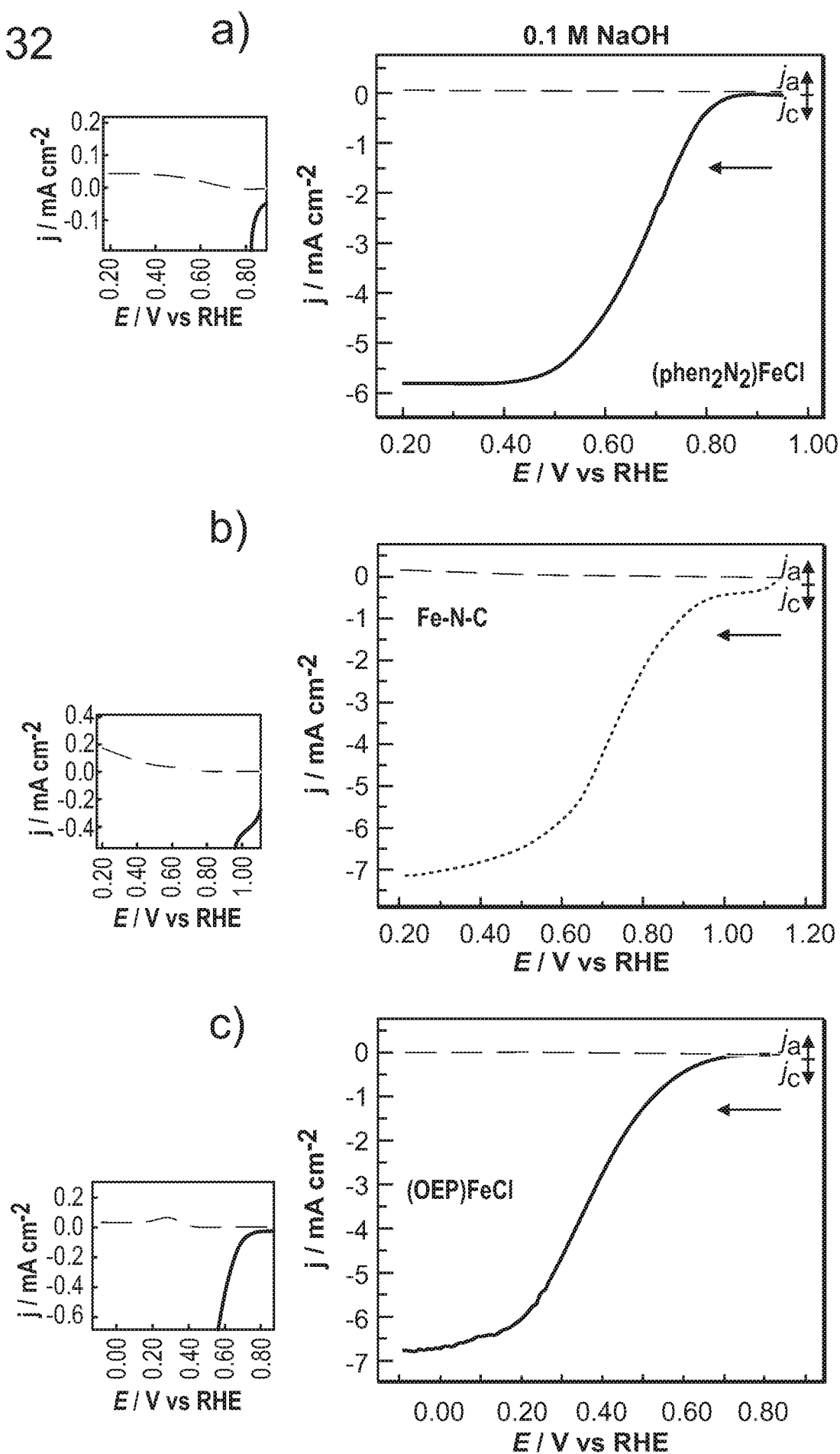


FIG. 33

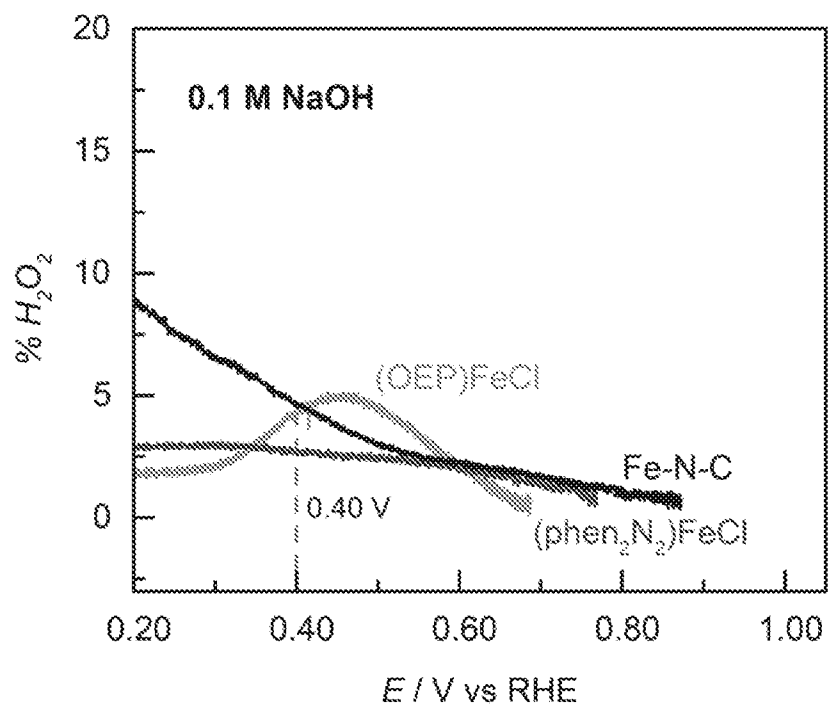


FIG. 34

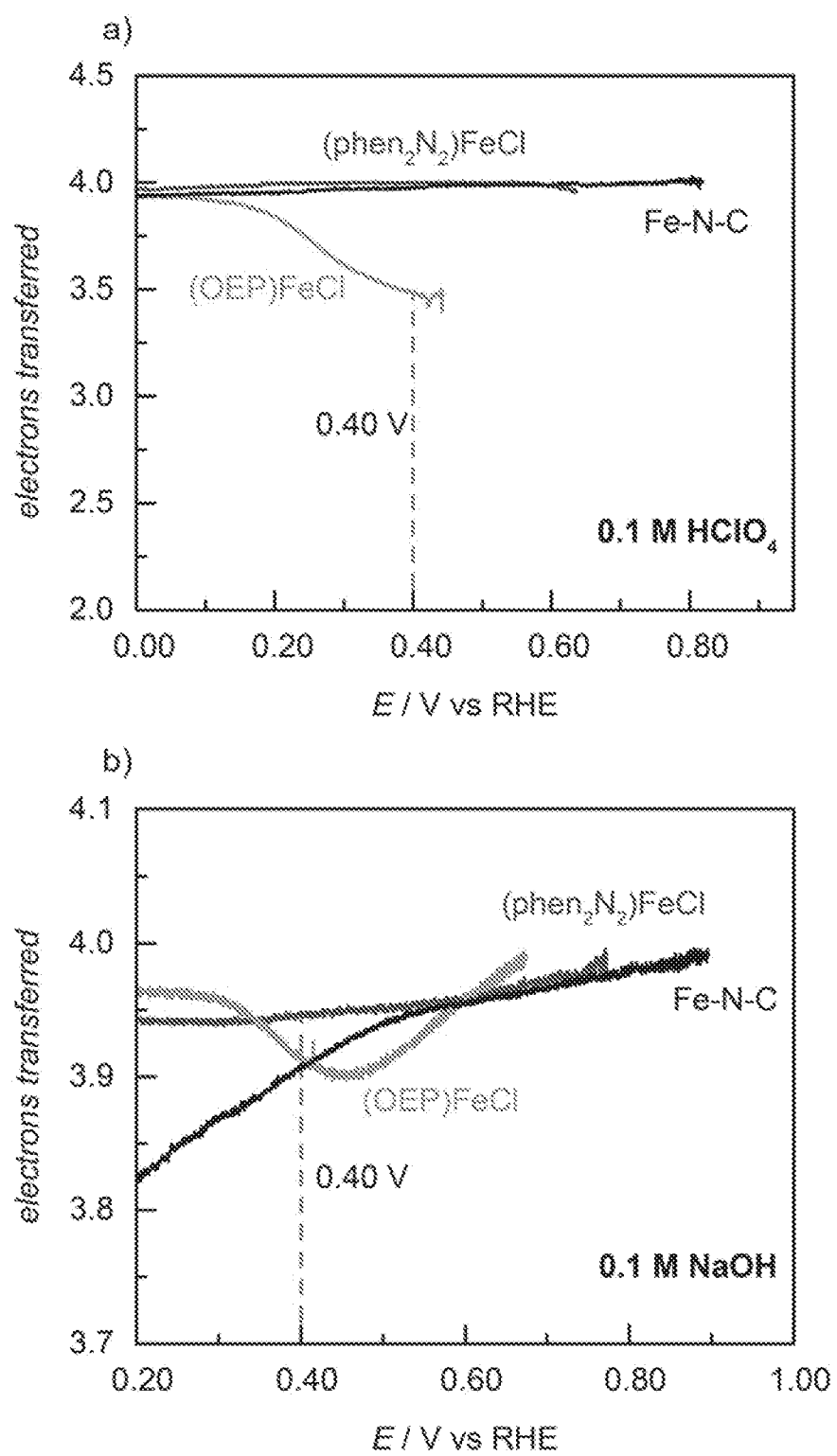


FIG. 35

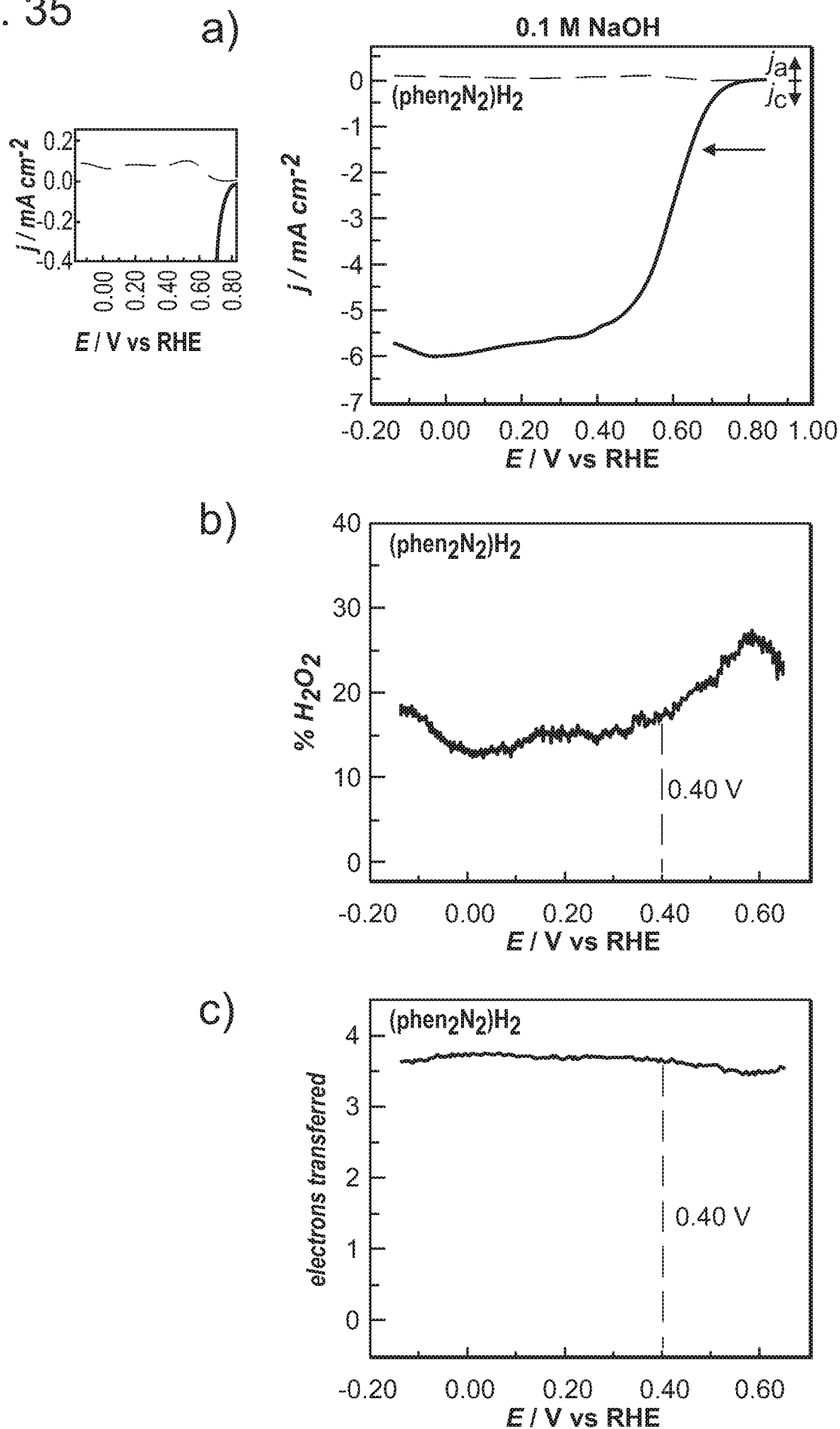
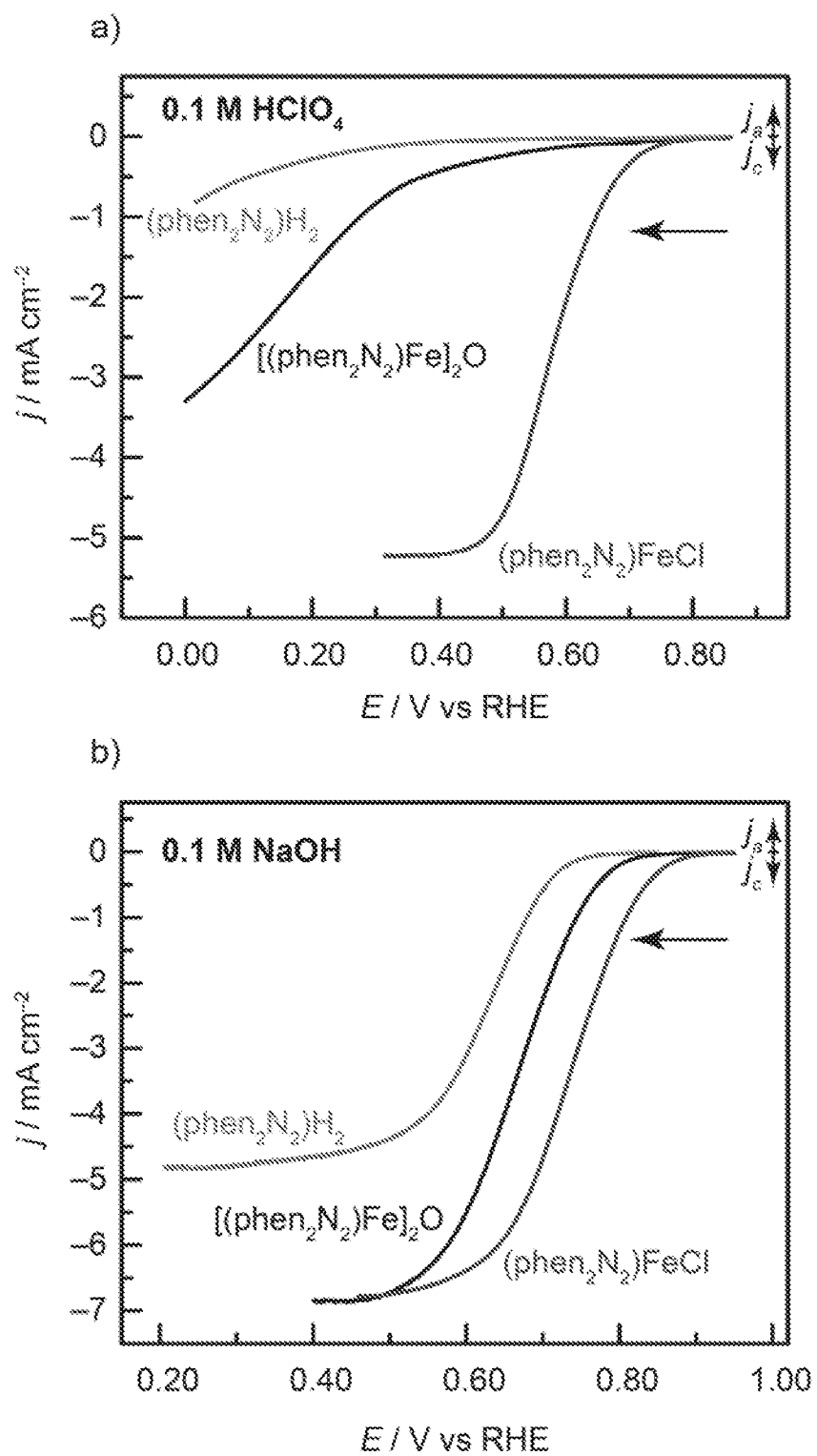


FIG. 36



3535/44

FIG. 37

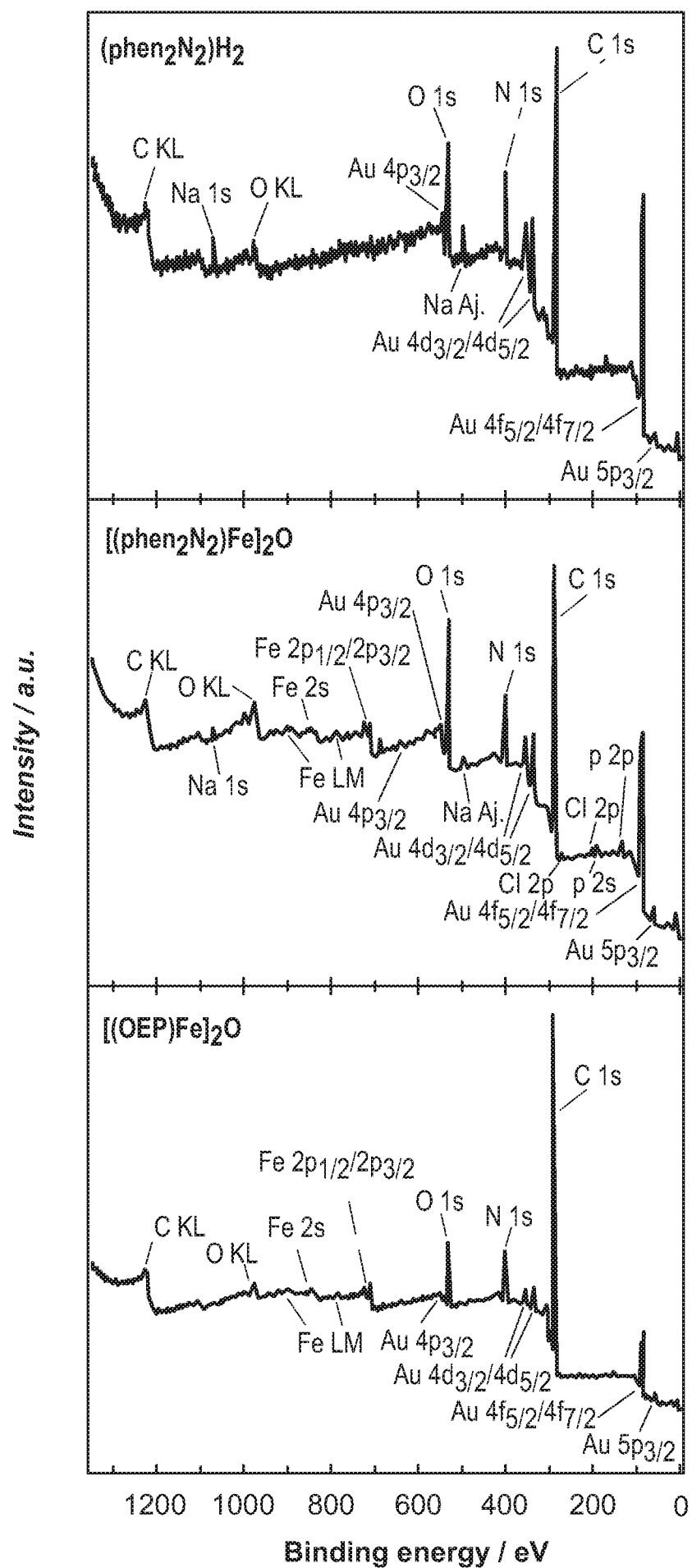


FIG. 38

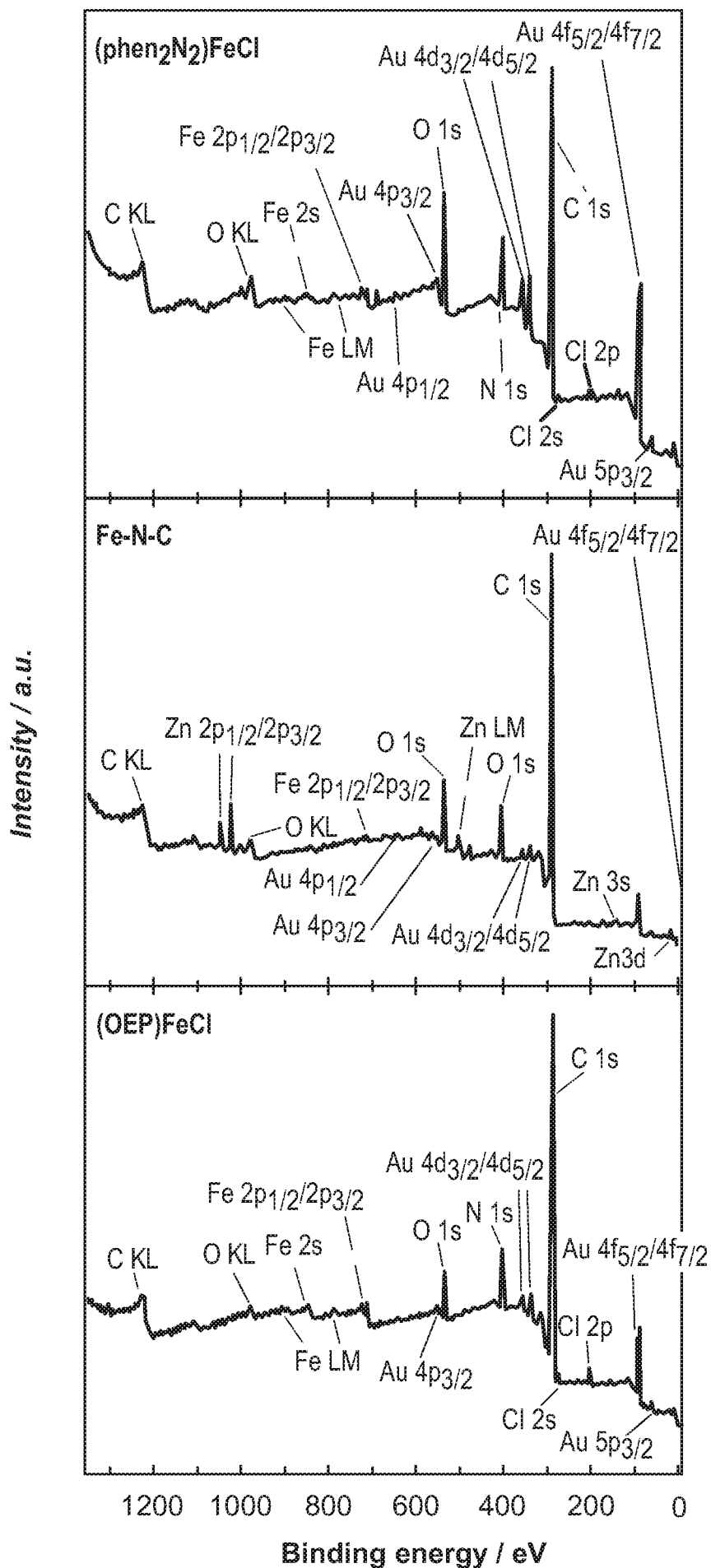


FIG. 39

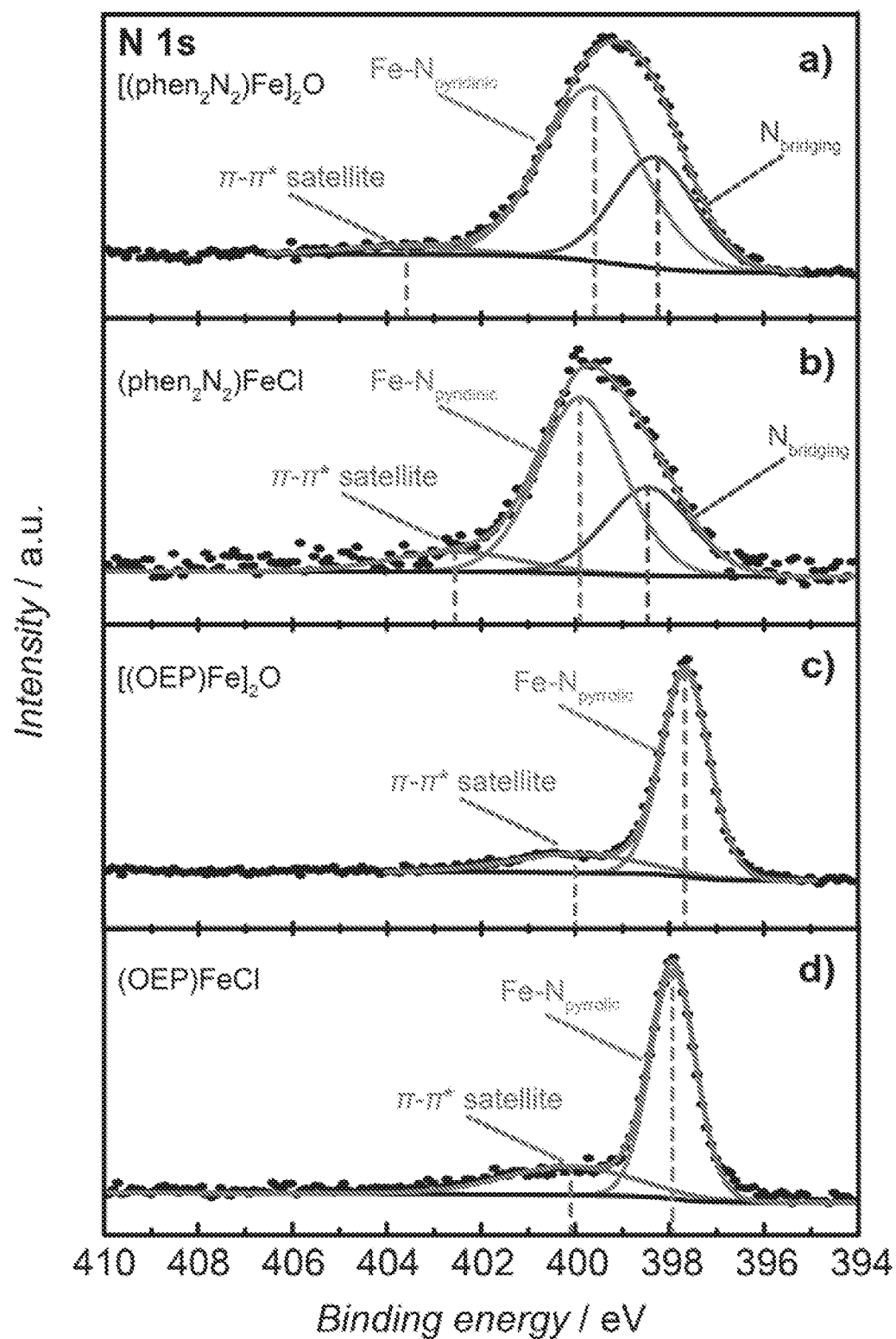


FIG. 40

	% Fe(II)	% Fe(III)
Fe-N-C	76.34	23.66

FIG. 41

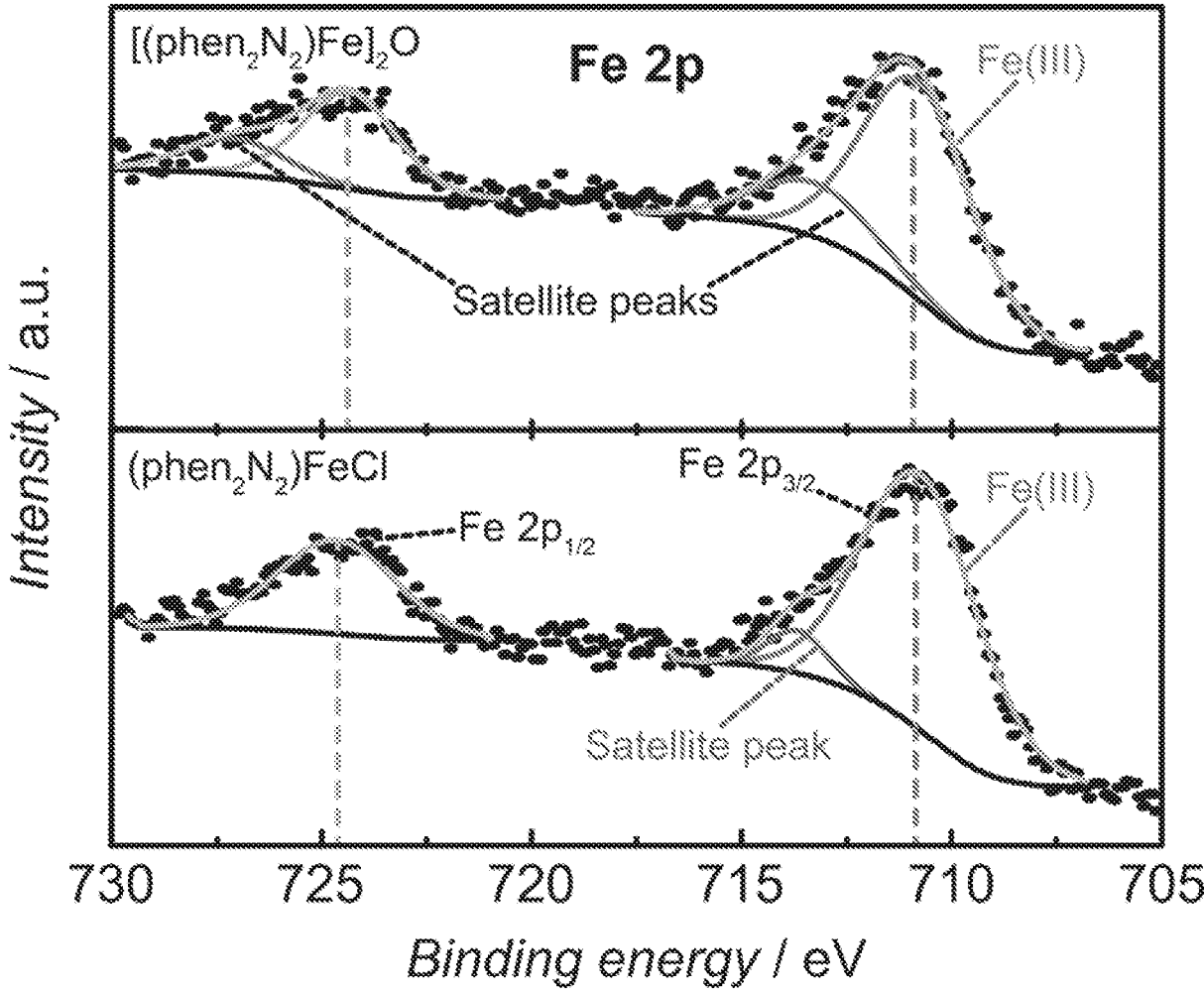


FIG. 42

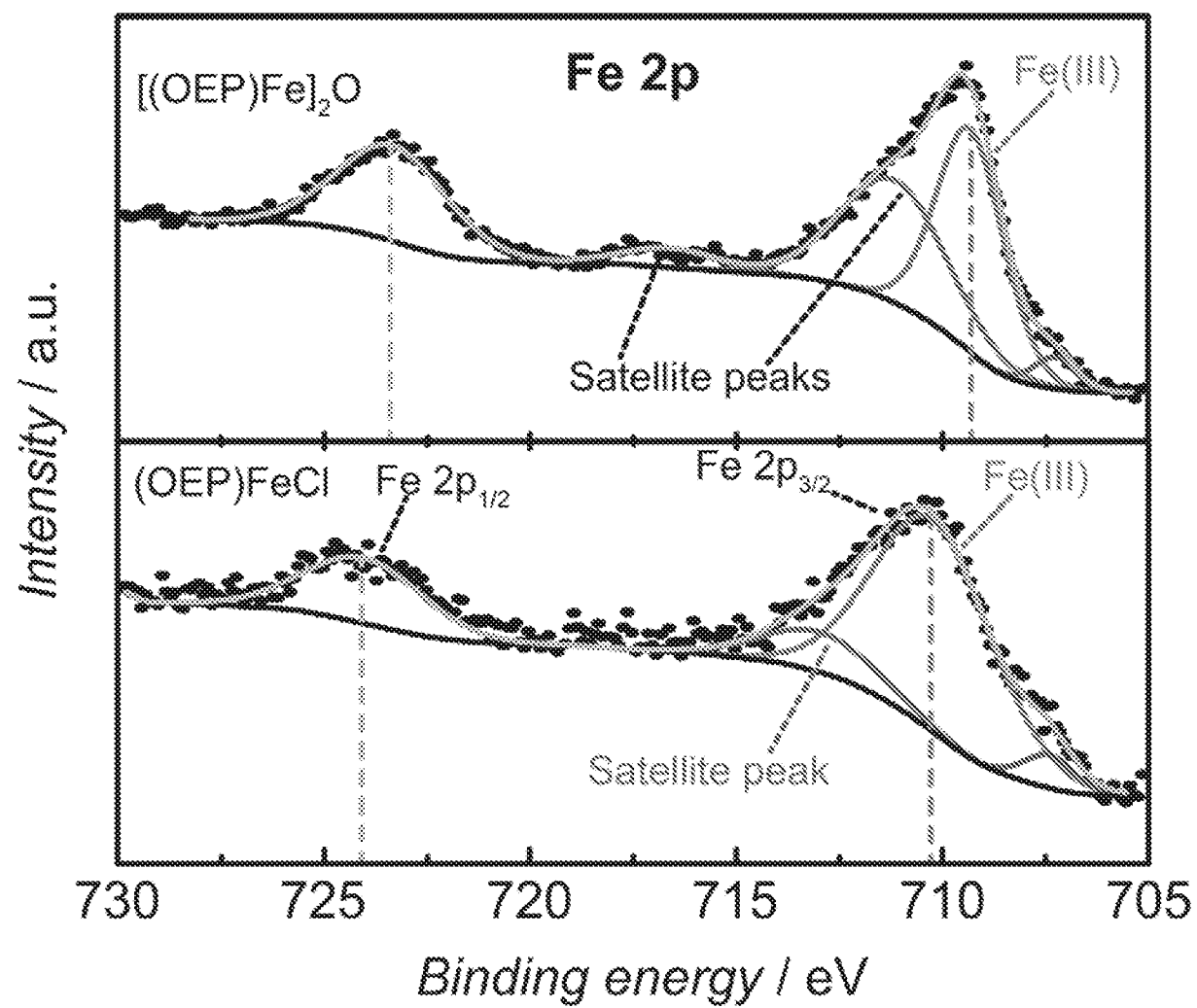


FIG. 43

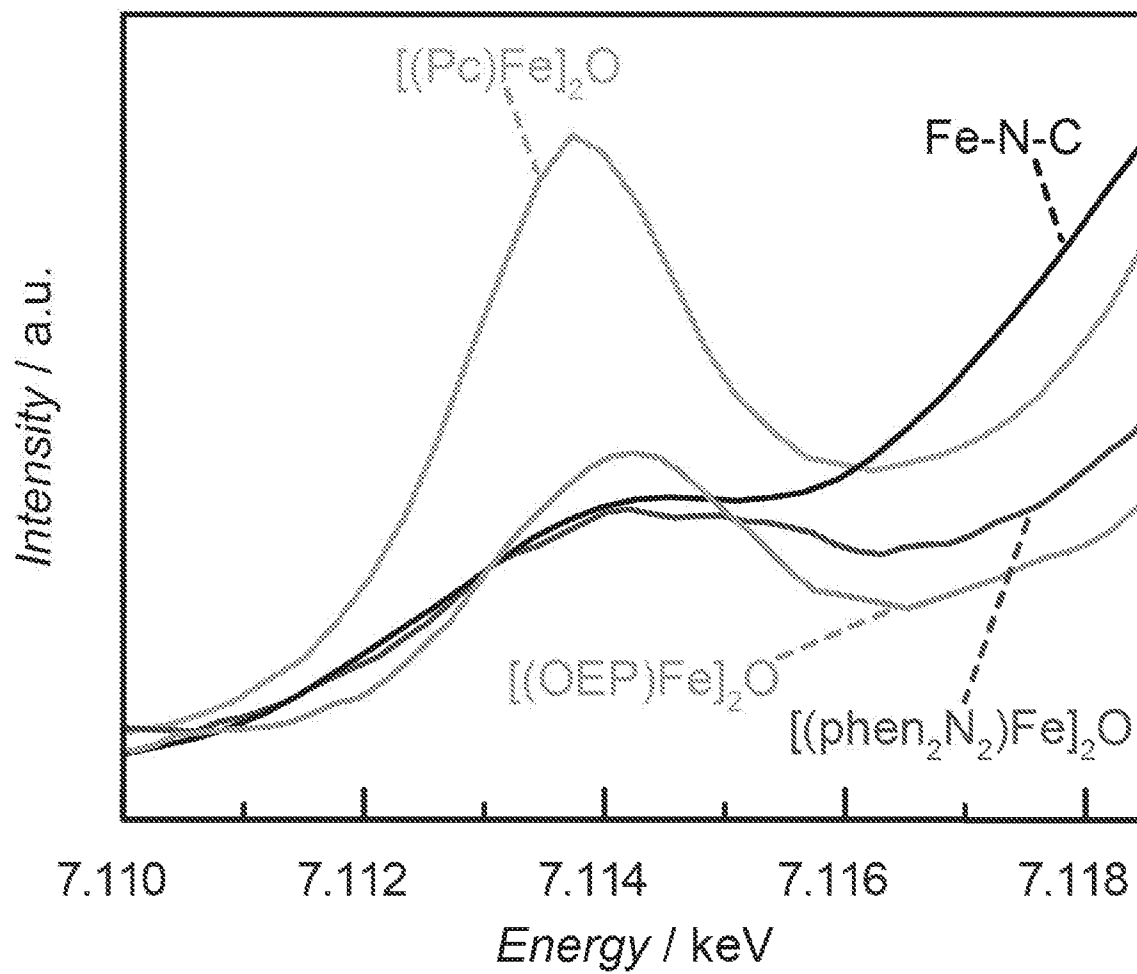


FIG. 44

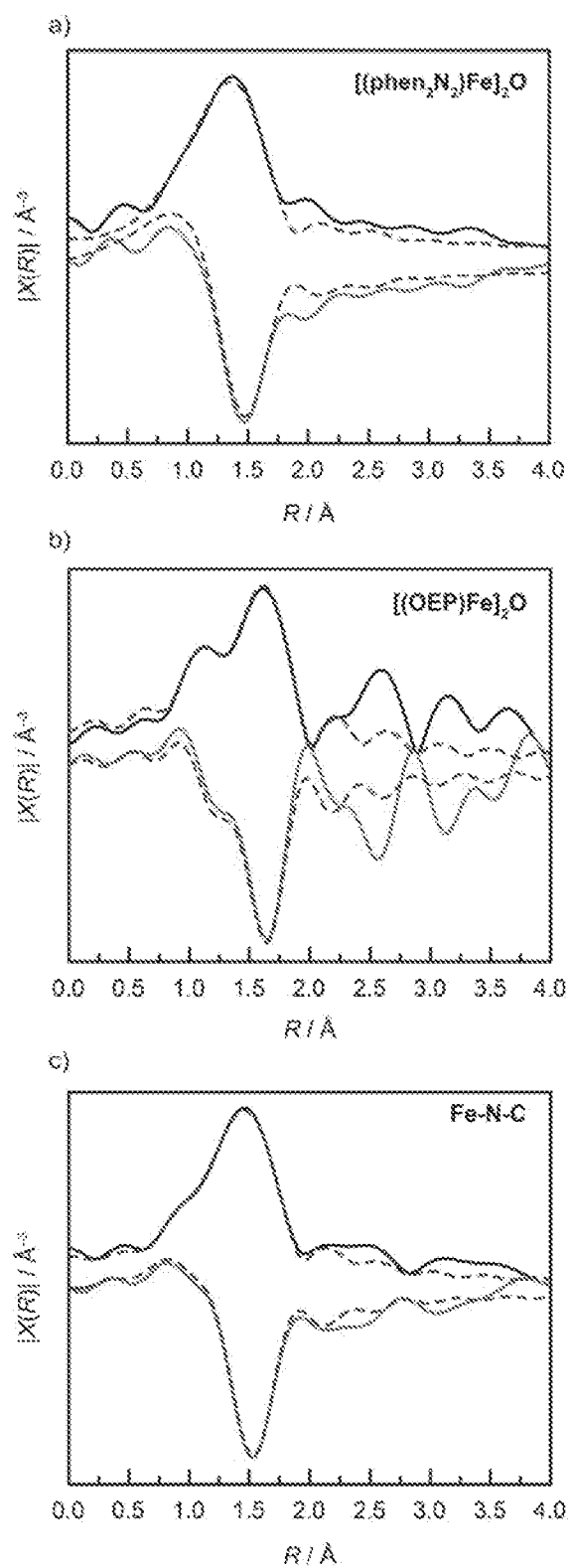
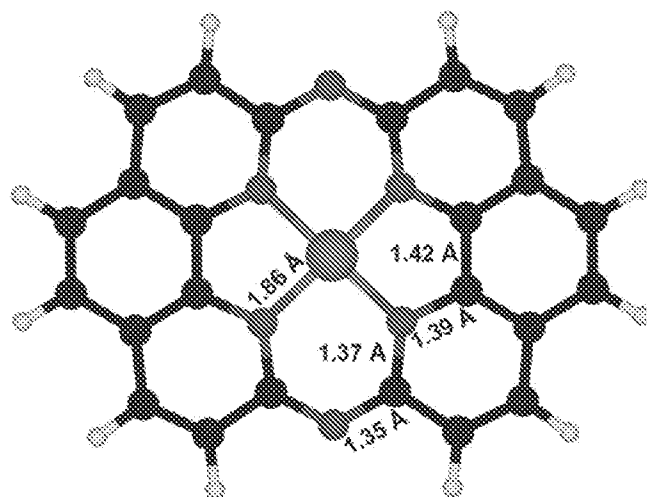


FIG. 45

$[(\text{phen}_2\text{N}_2)\text{Fe}(\text{III})]^+$ - top view



$[(\text{phen}_2\text{N}_2)\text{Fe}(\text{III})]^+$ - side view



FIG. 46

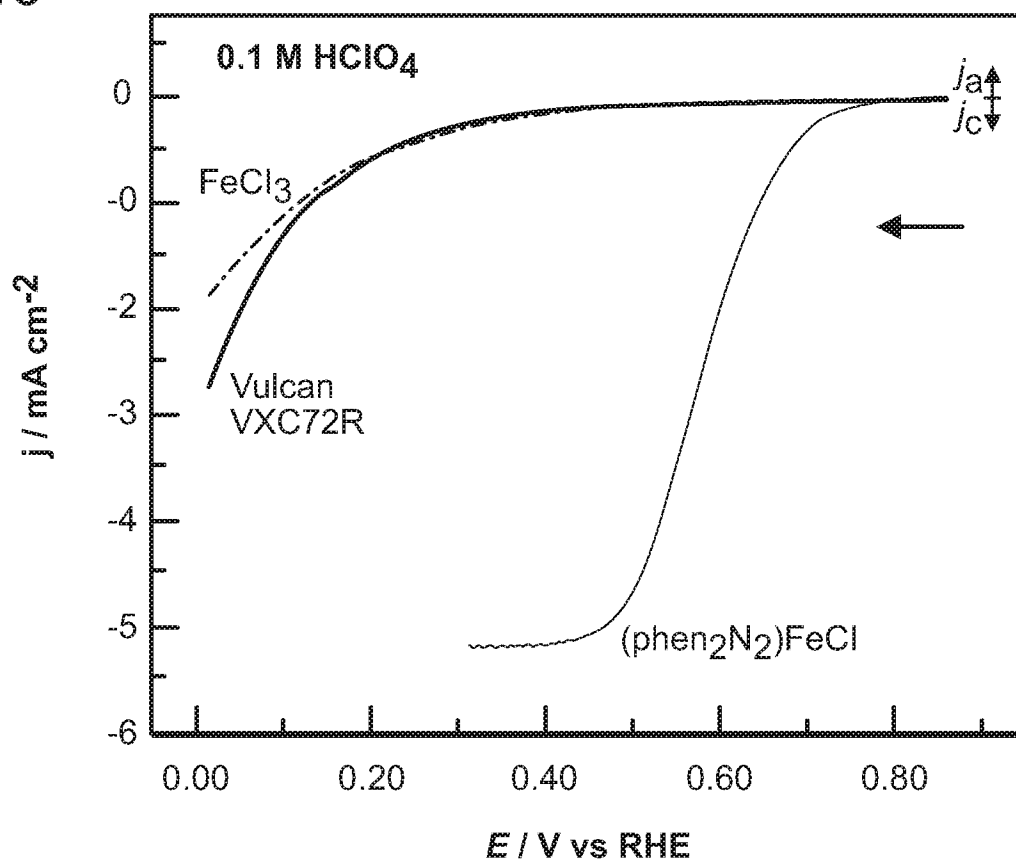


FIG. 47

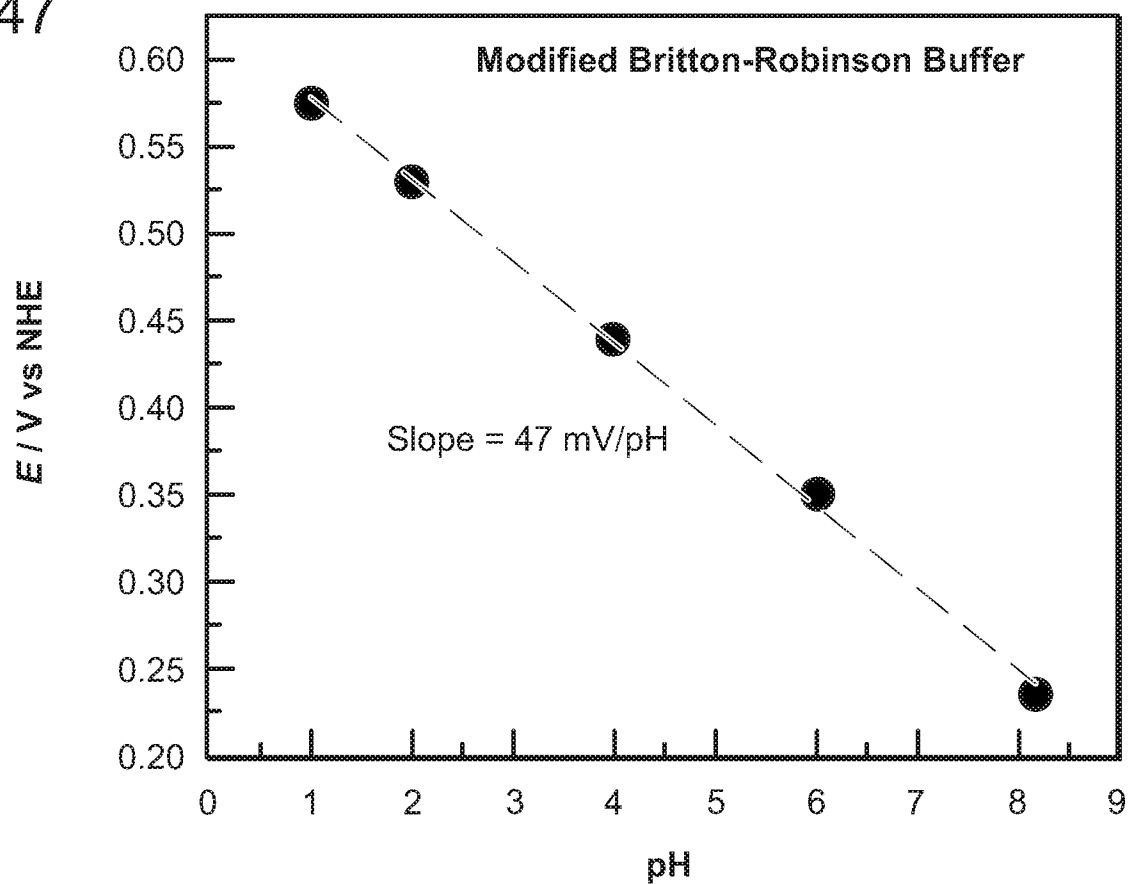


FIG. 48

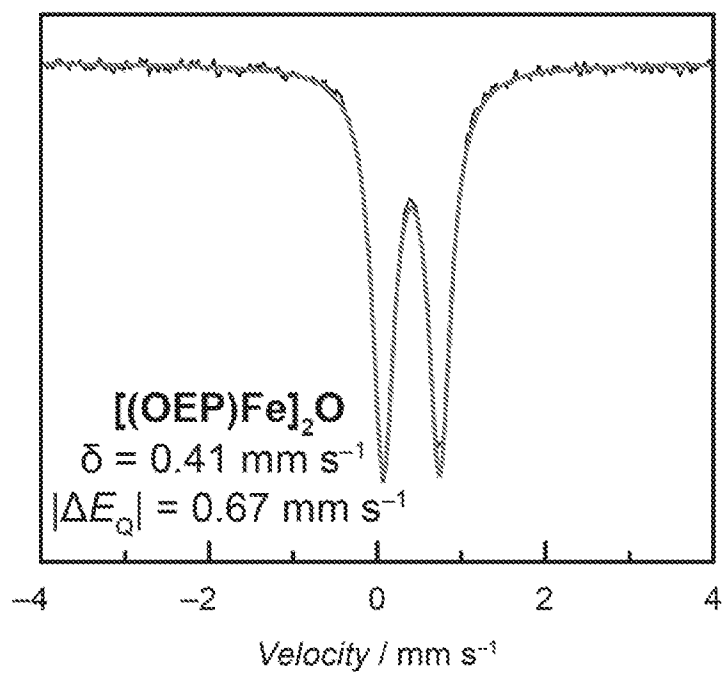
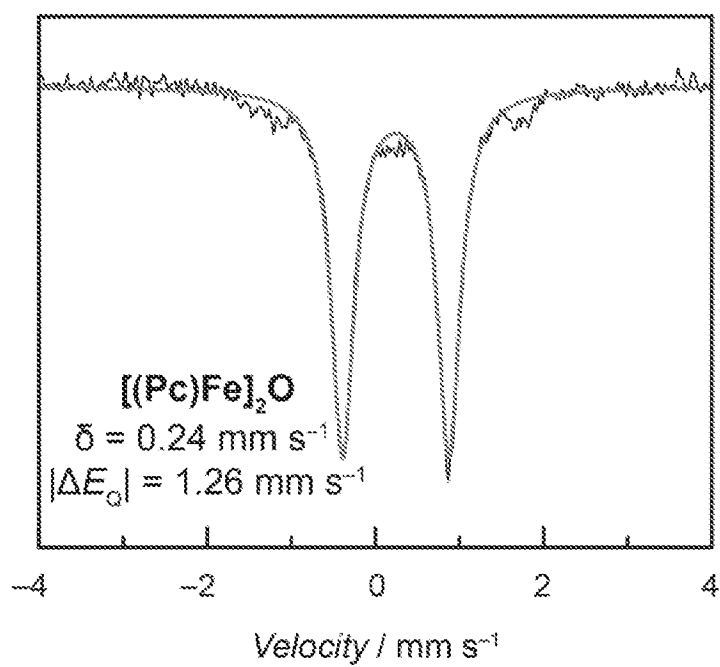


FIG. 49



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 20/22971

A. CLASSIFICATION OF SUBJECT MATTER

IPC - B01J 31/16; B01J 31/18; C07C 209/02 (2020.01)

CPC - B01J 31/1691; B01J 31/18; B01J 31/1815; C07C 209/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2012/169548 A1 (SUMITOMO et al.) 13 December 2012 (13.12.2012), entire document, especially: pg 12, para 13; pg 47, top, formula B-II-53.	1,5-6,14,26
A	US 2002/0095029 A1 (CHENG et al.) 18 July 2002 (18.07.2002), entire document.	1,5-6,14,26
A	PubChem-CID-44157885, Create Date: 24 August 2009 (24.08.2009), pg 2, Fig.	1,5-6,14,26
E/A	MARSHALL-ROTH et al. "A Pyridinic Fe-N4 Macrocyclic Effectively Models the Active Sites in Fe/N-Doped Carbon Electrocatalysts", ChemRxiv, 24 March 2020 (24.03.2020), doi.org/10.26434/chemrxiv.10008545.v2.	1,5-6,14,26

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"D" document cited by the applicant in the international application	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"E" earlier application or patent but published on or after the international filing date	"&" document member of the same patent family
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

6 July 2020

Date of mailing of the international search report

28 JUL 2020

Name and mailing address of the ISA/US

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Facsimile No. 571-273-8300

Authorized officer

Lee Young

Telephone No. PCT Helpdesk: 571-272-4300

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 20/22971

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 7-13, 16-19 and 30-41
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
--see attached extra sheet--

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1, 5-6, 14 and 26

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/US 20/22971

--BOX IV - LACK OF UNITY--

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I+: Claims 1-6, 14-15 and 20-29 directed to a compound of Formula I or a salt thereof. The compound of Formula I will be searched to the extent that it encompasses the first species of claim 1, wherein X1 and X2 are N; R3, R4, R5, R6, R7, R8, R9, R10, R11, R12, R13 and R14 are hydrogen. It is believed that claims 1, 5-6, 14 and 26 encompass this first named invention, and thus these claims will be searched without fee to the extent that they encompass the first species of claim 1. Applicant is invited to elect additional compounds of Formula I, wherein each additional compound elected will require one additional invention fee. Applicants must specify the claims that encompass any additionally elected compound. Applicants must further indicate, if applicable, the claims which encompass the first named invention, if different than what was indicated above for this group. Failure to clearly identify how any paid additional invention fees are to be applied to the "+" group(s) will result in only the first claimed invention to be searched. Additionally, an exemplary election wherein different actual variables are selected is suggested. An exemplary election would be a compound of claim 1, wherein X1 is C(R15) and X2 is N; R3, R4, R5, R6, R7, R8, R9, R10, R11, R12, R13, R14 and R15 are hydrogen (i.e. claims 1-2, 6, 20 and 22).

The groups of inventions listed above do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features:

Group I+ includes the technical feature of a unique compound of Formula I, which is not required by any other invention of Group I+.

Common technical features:

The inventions of Groups I+ share the technical feature of a compound having the structure of Formula I.

These shared technical features, however, do not provide a contribution over the prior art, as being anticipated by WO 2012/169548 A1 to Sumitomo Chemical Company (hereinafter 'SUMITOMO'). Sumitomo discloses a compound of Formula I wherein X1 and X2 are C(R15); R3, R4, R5, R6, R7, R8, R9, R10, R11, R12, R13, R14 and R15 are hydrogen (pg 47, top, formula B-II-54; see also pg 12, para 13, The central metal of the mononuclear metal complex is preferably a transition metal atom belonging to the fourth period to the sixth period of the periodic table or an ion thereof ...more preferably at least one selected from the group consisting of vanadium, chromium, manganese, iron, cobalt, nickel, and copper).

As said compound was known in the art at the time of the invention, this cannot be considered a special technical feature that would otherwise unify the inventions of Group I+.

The inventions of Group I+ thus lack unity under PCT Rule 13.

Note reg. item 4: Claims 7-13, 16-19 and 30-41 are unsearchable because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).