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2021

Wang, X., Zheng, T., Tang, Y., Li, X., Rykov, A. I., Li, X., Wang, J., He, Q., Cheng, J. & Zhang, X. (2021). The effect of tuning the coordination sphere of iron complexes for the oxygen reduction reaction in acidic media. *Journal of the Electrochemical Society*, 168(4), 044506-. <https://dx.doi.org/10.1149/1945-7111/abf21b>

<https://hdl.handle.net/10356/153574>

<https://doi.org/10.1149/1945-7111/abf21b>

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The Effect of Tuning the Coordination Sphere of Iron Complexes for the Oxygen Reduction Reaction in Acidic Media

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As a type of important non-precious catalyst for the oxygen reduction reaction (ORR), the regulating role of a metal centre in metal-macrocycles and other complexes for activity has been extensively studied. However, a common guideline to explain the effect of peripheral coordinated-ligands has not been reached. Herein, a series of organic iron complexes (denoted as FeL, L = TAA, Pc, TPP, Corrole, Tim and Salen) were synthesized as ORR catalysts and an explicit relationship of structure-activity was constructed. The kinetic current density for these compounds was identified to follow the order of FeTAA > FePc > FeTPP > FeCorrole > FeTim > FeSalen. An electron-transfer number close to 4 was derived for all these complexes except for FeTim and FeSalen, implying a near complete reduction of oxygen to water. X-ray absorption near edge structure spectroscopy (XANES) and Mössbauer spectroscopy were used to probe the nature of the distinct activities by investigating the iron-centre electron structures. Density function theory (DFT) calculations were carried out to study the charge redistribution across the iron complexes. Novel activity descriptors including the charge and spin densities on the Fe site were proposed and validated by available experimental data, presenting a strategy to design highly-active nonprecious metal complex catalysts with specific supporting ligands.

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Manuscript submitted January 29, 2021; revised manuscript received March 18, 2021. Published April 7, 2021.

Supplementary material for this article is available [online](#)

Proton exchange membrane fuel cells (PEMFCs) are considered as promising energy generation and utilization technologies that can ensure a safe, environmentally friendly and sustainable future.¹ However, the sluggish oxygen reduction reaction (ORR) is the bottle neck problem that has obstructed the development of many such fuel cell devices.²⁻⁴ Although platinum-based ORR catalysts, such as Pt/C, have been utilized to a certain extent, their low stability and high cost still block large-scale applications for PEMFCs.^{2,5} Therefore, it remains challenging to develop non-precious metal catalysts (NPMCs) with high activity and superior stability.⁵⁻⁷

In the past few years, NPMCs for the ORR have been the subject of extensive studies. In particular, transition metal (for example, Fe and Co) coordinated complexes have been demonstrated in many studies to exhibit promising ORR activities. Many researchers have developed metal complexes exhibiting a comparable activity to that of Pt-based materials in alkaline conditions. In addition, the activity of metal complexes is also gradually approaching that of platinum-based catalysts in acidic conditions.^{2,5,7,8}

Although great progress has been made in the ORR catalysed by metal complex catalysts, a considerable overpotential and low stability exist for these kinds of catalysts.^{9,10} The traditional strategy to improve the catalytic performance of metal complex catalysts for ORR is to conduct a high-temperature pyrolysis process with carbon for converting a metal complex into M-N-C composites with an uncontrollable structure and inevitable agglomeration.¹⁰⁻¹³ Furthermore, the nature of the active sites in heat-treated M-N-C catalysts remains unclear, which makes it difficult to achieve rational design of catalysts for ORR.¹⁴ In addition, current progress primarily involves an empirical approach based on trial-and-error for the complex structure, which leads to a low efficiency and limits further advances.¹² Therefore, rational design of catalyst materials requires proper understanding of the

mechanistic origin of the ORR and a reliable direction to theoretically construct effective complex structures for the development of non-noble catalysts.

It has been reported that the reactivity of metal complexes with O₂ is regulated by the nature of the transition metal ions.^{10,15-19} Ward et al.²⁰ studied a series of divalent metal complexes supported by the ligand tris(2-pyridylmethyl)amine ([TPA]M²⁺)ⁿ⁺, M = Mn, Fe, Co, Ni, and Cu) as oxygen reduction catalysts for fuel cell applications, and found that the iron-based complex exhibited the best catalytic activity. For the series presented, the metal centre appears to dictate the peroxide yield, and thus, the reaction kinetics. Zhang et al.¹⁵ reported a series of transition-metal phthalocyanines supported on graphitized carbon black (TMPc/GCB, TM: Fe, Co, Ni and Cu) for the oxygen reduction reaction and drew the conclusion that different adsorption and desorption pathways between metals and oxygen species are the major steps for determining ORR catalytic activity.

On the other hand, the metal centres do not exist in isolation, and the nature of the supporting ligand scaffolds may also play a key role in the electronic structure of metal ions via coordination sphere effects, thus affecting the reactivity of complexes with dioxygen.^{21,22} In fact, the indirect ligand coordination effect on catalytic activity has been proven to be quite important based on experiments and theories. Daniel et al.²³ developed the molecular scaling relationships for Fe-porphyrin to connect the thermochemistry, mechanism, and rate law for a O₂ reduction catalytic system. Baker et al.²⁰ prepared four phthalocyanine macrocycle -based iron complexes (FePc, FePc(SO₃H)₄, FePcCl₁₆, FeNpPc(tBu)₄) with different types of substituents, which can change the mode of O₂ adsorption and the electrochemical activity along with the stability by affecting the electron density of both the ring and in particular the metal centre. Li et al.²⁴ synthesized cobalt(III) triarylcorroles containing 1-3 nitro groups. Electrochemical characterization indicates that the more electron-drawing groups (nitro-substituents) on the cobalt corrole, the better the compound acts as a catalyst. The role of a

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π -conjugated ligand is demonstrated to modify the electronic structure of the metal ion by relocating its redox potential.^{25–27}

In addition, based on a molecular-orbital approach, the end-on M–O₂ interaction primarily involves bonding between molecular orbitals of O₂ and the transition metal ion.^{28,29} The gap between the HOMO energy of the metal ion and the LUMO energy of O₂ is defined as the intermolecular hardness of M–O₂ (η_{DA}).³⁰ Pearson et al. demonstrated that softer molecules (with smaller HOMO–LUMO energy gaps) react faster than harder molecules (with larger HOMO–LUMO energy gaps); hence, η_{DA} was proposed as an activity descriptor for ORR catalysts, which is related to the redox potential of the metal centre. Furthermore, substitution of electron withdrawing groups on the coordination sphere can bring about a downshift for e_g -orbitals,³¹ increasing the bond strength between the metal centre and ORR intermediates, leading to a softer M–O₂ molecule and an anodic shift of the redox potential, thus showing a higher turnover number and catalytic activity.^{32,33}

Despite these studies with coordination compounds for the ORR, both in homogeneous and heterogeneous configurations,^{21,22} a consensus for the explicit role of the different supporting ligand species in the electronic and coordination structure of metal centres, as well as the ORR activity of metal complexes, has not been reached. For moving the cognition forward, the identification of the coordination sphere effect and a bottom-up design strategy for the rational structure of metal complex catalysts is needed. As such, we prepared a series of iron complex catalysts with different ligands including macrocyclic, cyclam derivatives and Schiff base ligands (FeTAA, FePc, FeTPP, FeCorrole, FeTim, and FeSalen), which have been proven effective for ORR in the literature.^{7,11,20,34–36} We compared their electrochemical catalytic performance and deciphered the nature of the observed difference in the activity by investigating the iron-centre electron structures using X-ray absorption near edge structure spectroscopy (XANES) and Mössbauer spectroscopy. Furthermore, we carried out structure-optimized DFT calculations for these molecules and presented simple descriptors for these transition metal complexes, which is expected to provide some insight into a possible mechanism for oxygen activation and a proper design strategy for the molecular structure of an ORR catalyst.

Experimental

Materials.—FeTPP (Sigma-Aldrich Co., USA) and FePc (Sigma-Aldrich Co., USA) were used as received. Other iron complexes, as shown in Fig. 1, were synthesized accordingly,^{25,34,37–39} and the details for the synthesis are introduced in the supporting information. The identity of self-prepared samples has also been confirmed by ¹H NMR (MercuryPlus 400 NMR spectrometer, Varian) in Fig. S1 (available online at stacks.iop.org/JES/168/044506/mmedia). Element analysis was conducted using a Vario EL cube (Elementar Co., Germany). The experimental data are listed in Table S1. By comparison with calculated results, the structures for these synthesized compounds were identified.

A general ink preparation method and uniform electrochemical measurement method for these iron complex catalysts was introduced as below, which guaranteed the consistent role of carbon powder, ionomer and acidic medium in the iron coordination environment for the heterogeneous samples. 10 mg of a certain catalyst and 10 mg of Vulcan-72 carbon were stirred in 40 ml of ethanol for 18 h. Then, the solvent was removed under vacuum. Next, 10 mg of carbon supported iron complex catalysts was dispersed in 2 ml of deionized water and 0.75 ml of isopropanol. Finally, 40 μ l of Nafion solution (5%) was added before ultrasonic mixing.

Electrochemical characterization.—Electrochemical measurements for the non-pyrolyzed transition metal complex electrocatalysts have been reported in the literature.^{15,40} Following the similar procedure, cyclic voltammetry and rotating disk electrode (RDE) experiments for different iron complex samples were carried out in a

three-compartment cell using an Autolab potentiostat (PGSTAT204N). 20 μ l of catalyst ink was drop cast onto a glassy carbon electrode (diameter 5 mm) obtained from Metrohm AG, which was used as the working electrode at room temperature. A reversible hydrogen electrode (RHE) was used as the reference electrode and a graphite rod was used as the auxiliary electrode. Cyclic voltammetry (CV) was carried out in 0.1 M HClO₄ solution saturated with either argon or oxygen at room temperature. All RDE experiments were conducted in 0.1 M HClO₄ saturated with oxygen.

X-ray absorption spectroscopy (XAS).—Fe K-edge X-ray absorption near-edge structure (XANES) spectra of powder iron complexes were recorded at room temperature in transmission mode at the beamline BL14W1 of the Shanghai Synchrotron Radiation Facility (SSRF). The raw data analysis was performed using the IFEFFIT software package according to the standard data analysis procedures. The spectra were calibrated, averaged, pre-edge background subtracted, and post-edge normalized using the Athena program in IFEFFIT software package.

Mössbauer spectroscopy.—The ⁵⁷Fe Mössbauer spectroscopic studies were carried out at the Center for Advanced Mössbauer Spectroscopy at Dalian Institute of Chemical Physics using a Mössbauer spectrometer (MFD-500AV-02, Topologic Systems, Inc.). The spectra were measured with a ⁵⁷Co:Rh source. The spectrometer was operated with a triangular velocity waveform. The source and absorber were held at room temperature during the measurement. A standard Fe foil was used to calibrate the velocity.

DFT calculations.—All DFT calculations were performed with the Gaussian 09 software package.^{41,42} We considered different electronic configurations for all molecular geometries and the most stable configurations are given in this article. Gas phase calculations for all molecular geometries were carried out by using the Becke 3-parameter hybrid exchange and Lee–Yang–Parr correlation functional (B3LYP)^{42,43} together with Grimme’s dispersion correction D3(BJ).⁴⁴ The basis set Lan2dz⁴⁵ was used for the Fe atom, and a split valence double- ζ basis set with extra polarization and diffuse functions (6–31+G(d,p)) was used for all other atoms. Solvation energies for all molecular geometries were computed with the CPCM model⁴⁶ to account for solvation effects (water) using the same functional and basis sets with the gas phase calculations. The solvation calculations omitted empirical non-electrostatic energy contributions (cavitation, dispersion, repulsion).⁴⁷ Zero-point energies, the total thermal and entropic energies were corrected using the standard harmonic oscillator, ideal gas, and rigid rotor approximations. Frequency calculations with the same parameters were also performed to identify all of the optimized geometries as actual minima on the potential energy surface (zero imaginary frequencies) and to provide Gibbs free energies at the default temperature of 298.15 K and an atmospheric pressure, which included entropic contributions by taking into account the vibrational, rotational, and translational motions of the species under consideration. The charge transfer between the catalytic molecule and the adsorbates was obtained through charge analysis by using the natural population analysis (NPA) method based on natural bond orbital (NBO) theory.⁴⁸

Results and Discussion

Cyclic voltammetry was conducted in 0.1 M HClO₄ with saturated Ar and O₂ (See Fig. S2). Compared with CV curves in an Ar-saturated solution, CV curves conducted in O₂-saturated 0.1 M HClO₄ all exhibit obvious reductive peaks suggesting the reduction of dioxygen. The onset potential is one of the most important metrics for characterization of ORR catalytic film activity.^{49,50} The positive shift for this potential represents a better electrochemical catalytic performance for ORR. From Fig. S2 and Table 1, the oxygen reduction onset potential follows the sequence of

Figure 1. Schematic structures of Fe-based complexes with different coordination ligands.

FeTAA > FePc > FeTPP > FeCorrole > FeTim > FeSalen, which is consistent with the activity sequence indicated by the RDE results discussed in the following.

The results from RDE experiments carried out on a glassy carbon electrode coated with an iron complex catalyst in oxygen-saturated 0.1 M HClO₄ are shown in Fig. S3. The polarization curves for the six carbon-supported iron complex catalysts mentioned above at 900 rpm are displayed in Figure 2a. The half-wave potential ($E_{1/2}$) for the polarization curve was generally applied to describe the catalytic activity, and the positive shift for $E_{1/2}$ suggests better catalytic activity.^{49,50} The half-wave potentials for the six catalysts in our study are summarized in Table I, and the catalytic activity was found to follow the sequence of FeTAA > FePc > FeTPP >

FeCorrole > FeTim > FeSalen. A similar order of turn-over frequency calculated with Eq. 1 for different Fe-based catalysts can be found in Fig. S4.

$$TOF = \frac{j_k}{\frac{W_{Fe}}{M_{Fe}} \times N_A \times m_{loading}} \quad [1]$$

Where W_{Fe} and M_{Fe} ($|M_{Fe}| = 55.85 \text{ g mol}^{-1}$) are the mass fraction and molar weight of Fe, respectively. j_k is the mass transfer corrected kinetic current density. N_A is Avogadro's number ($6.02 \times 10^{23} \text{ mol}^{-1}$). $m_{loading}$ is the loading mass of iron complex per unit of electrode area.

Figure 2. (a) Rotating disk electrode (RDE) ORR polarization plots (b) Tafel plots collected for iron complexes adsorbed onto Vulcan-72 carbon in O₂-saturated 0.1 M HClO₄ at 20 mV·s⁻¹ with a rotation rate of 900 rpm at room temperature.

Table 1. Comparison of the electrochemical data obtained for FeTAA, FePc, FeTPP, FeCorrole, FeTm and FeSalen.

Sample	E_{onset}/V vs RHE	$E_{1/2}/V$ vs RHE	Number of exchanged electrons [n]	Tafel slope/mV.dec ⁻¹	$\mathbf{Fe}^{(O)}/\mathbf{Fe}^{(R)}$	transition potential/V vs RHE
FeTAA	0.82	0.69	3.77	56/127		0.86
FePc	0.79	0.57	4.01	59/116		0.84
FeTPP	0.69	0.37	3.90	191		0.80
FeCorrole	0.64	0.28	3.83	145		0.76
FeTm	0.62	0.26	3.10	142		0.67
FeSalen	0.44	0.16	3.06	158		0.60

Figure 3. (a) XANES spectra for iron complex compounds, (b) the relationship between the ORR half-wave potential in 0.1 M HClO₄ electrolyte vs pre-edge intensity in the XANES spectra and isomer shift in Mössbauer spectroscopy for iron-based complex catalysts.

To further study the electron-transfer number for oxygen reduction, Koutecky-Levich plots were obtained according to Eqs. 2 and 3:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} \quad [2]$$

$$j_d = 0.620nFD\frac{2}{3}C_O\nu^{-\frac{1}{6}}\omega^{\frac{1}{2}} \quad [3]$$

where j is the current density (A·cm⁻²), j_d is the diffusion-limiting current density, n is the number of electrons for the reaction, F is the Faraday constant (96,485 C·mol⁻¹), D is the diffusion coefficient for O₂ in the solution (2.0×10^{-5} cm²·s⁻¹), ν is the kinematic viscosity of the solution (0.01 cm²·s⁻¹), C_O is the O₂ concentration in the oxygen-saturated solution (1.25 mM), and ω is the angular frequency of rotation.

K-L plots are displayed in Fig. S5 and the transfer electrons for iron complexes are also summarized in Table I. FeTAA, FePc, FeTPP and FeCorrole were found to exhibit an electron-transfer number close to 4, suggesting a complete 4e⁻ oxygen reduction to H₂O, while the values for n derived from the K-L plot for FeTim and FeSalen were near 3, respectively, implying an incomplete reduction of oxygen to peroxide. This manifests that the ligand structure in iron complex catalysts, modulating the electron structure in iron centre, can affect not only the catalytic activity but also the reaction pathways for ORR.

To obtain more information regarding the ORR kinetics and mechanisms, Tafel plots for the above catalysts were constructed, as shown in Figs. 2b and S6. Accordingly,⁵¹ at low polarizations, preceded by a reversible one-electron one-proton transfer step as Eq. 4, the following Eq. 5 was proposed for the rate-determining step for the ORR catalysed by Fe-based complexes in acidic media:

$$slope = -0.060 \text{ V dec}^{-1}$$

At higher polarizations, a different rate-determining step can be proposed, as shown by Eq. 6, and the Tafel slopes change to a larger value.

$$slope = -0.120 \text{ V dec}^{-1}$$

where the $Fe^{(O)}$ species represents the high-valent iron with oxidation state and the $Fe^{(R)}$ species means the low-valent reduction form. As Eq. 4 has shown, the first step is about the transition process from $Fe^{(O)}$ to $Fe^{(R)}$, thus the reduction potential for $Fe^{(O)}$ species is directly relating to the onset potential for ORR.⁵² In our study, the onset potential for $Fe^{(O)}/Fe^{(R)}$ transition from the CV curves (Fig. S2) are listed in Table I and its sequence is found consistent with the ORR onset potential.

Furthermore, in order to get more information regarding ORR kinetics and mechanisms, Tafel plots were constructed in Fig. S6 and the slope values were displayed in Table I. A potential-dependent Tafel plot was observed for FeTAA and FePc, respectively. At the lower overpotential regions, the Tafel slopes for FeTAA (56 mV dec⁻¹) and FePc (59 mV dec⁻¹) approach 60 mV dec⁻¹, indicating a rate-determining step that follows Eq. 5. In addition, at a higher overpotential, the Tafel slopes for FeTAA (127 mV dec⁻¹) and FePc (116 mV dec⁻¹) are near 120 mV dec⁻¹, which suggests that Eq. 6 can express the determining step for the oxygen reduction process. For the other four catalysts, the Tafel slopes were found to be potential-independent. A Tafel slope of approximately 150 mV dec⁻¹ implied a similar reaction mechanism for FeCorrole (145 mV dec⁻¹), FeSalen (158 mV dec⁻¹) and FeTim (142 mV dec⁻¹). A much larger Tafel slope of 191 mV dec⁻¹ for FeTPP has also been reported,⁵³ which may result from a combination of factors, such as: (i) intrinsic properties of the oxygen reduction mechanism and the reaction order of oxygen for the FeTPP catalyst^{54,55} (ii) incomplete catalyst utilization at high overpotentials.⁵³

To probe the origin of the difference in the electrochemical catalytic activity, ex situ X-ray absorption near edge structure (XANES) measurements have been widely carried out to investigate the relationships between electron structure of the metal centre and ORR activity for homogeneous and heterogeneous catalysts.^{9,10,14} The whole XANES spectra for all six iron complexes are displayed in Fig. 3a. It is noticed that these iron-based complexes exhibit different K-edge positions and white line intensities relevant to the density of the unoccupied state in the metal centre, representing the diverse oxidation state of the Fe ions. The pre-edge peak represents an s-d like transition, and is, thus, dipole-forbidden, but it becomes partially allowed by mixing of the d-states of the transition metal with the p-states of the surrounding atoms. This means that the pre-edge peak energy position and intensity depend strongly on the mean Fe oxidation state and on the geometry around the Fe atom.^{52,56} In particular, accurate evaluation of the pre-edge peak energy position

Table II. Parameters for XANES and Mössbauer spectroscopy for iron complexes.

Sample name	Pre-edge peak position in XANES/eV	Integrated pre-edge peak intensity in XANES	Isomer shift in Mössbauer spectroscopy/mm·s ⁻¹
FeTAA	7115.0	0.2171	0.36
FePc	7113.0	0.2063	0.35
FeTPP	7114.0	0.2297	0.33
FeCorrole	7114.5	0.2827	0.28
FeTim	7113.4	0.1823	0.3
FeSalen	7113.8	0.1789	0.3

and integrated intensity can provide reliable information for both the Fe oxidation state and coordination environment.^{57,58} The magnified pre-edge peaks in the XANES spectra are also displayed in Fig. S7, and Table II lists the pre-edge peak data for the six iron complexes. A more positive pre-edge position seen on FeTAA than other macrocycles and complexes, representing the case in which a surrounding ligand produces an Fe centre with a higher oxidation state, may help to promote its electro-catalytic activity for ORR.

Furthermore, we plot the ORR half-wave potential vs pre-edge peak intensity for these Fe complex catalysts in Fig. 3b. It indicates that the oxygen activation can be boosted as the pre-edge peak intensity increases, which may be attributed to the higher Fe oxidation state and generally enhanced deformation of the square planar structure in the iron complexes. As an exception, FeCorrole contains a super high-valent iron centre, governed by more ionizable protons in the corrole N₄-coordination core.⁵⁹ The k3-weighted Fourier transform spectra from EXAFS for these studied iron complexes have also been displayed in Fig. S8. From EXAFS fitting results of the shells in Table SII, the coordination numbers of iron site are similar with the schematic structures of iron complexes in Fig. 1, which proves that their constructions exist as designed.

⁵⁷Fe Mössbauer spectroscopy has proven to be a powerful technique for identifying the coordination environments, oxidation and spin states of Fe atoms in iron complexes.⁶⁰ Important information for the electronic properties of active sites in catalysts^{61,62} and insights into the mechanisms involved for the catalytic process can be obtained.^{63,64} Mössbauer spectroscopy and its deconvolution for all six iron complexes are displayed in Fig. 4. An similar symmetrical doublets are observed for FeTAA and FeCorrole, which is attributed to a Fe-N₄ component. The Mössbauer spectrum of FePc consists of two doublets assigned to Fe²⁺ and Fe³⁺, which is consistent with the previous reports.^{65,66} According to the literature,^{67,68} the asymmetric doublet for a Fe-Salen sample can be caused by off-diagonal hyperfine interactions. For FeTPP and FeTim, a singlet implies the existing superparamagnetic component.⁶⁹ Accordingly,⁷⁰ the isomer shift is due to the electric monopole interaction and is related to the 4s electron density of iron at the nucleus, and, indirectly (via a shielding effect) to the 3d electron density; also, the isomer shift increases gradually from a low-spin to high-spin state for Fe-N₄ sites. The following Eq. 7 gives a mathematic description for an isomer shift δ_{iso} .

$$\delta_{iso} = 2/5\pi(Z \cdot e^2)(R_E^2 - R_G^2)(|\Psi(0)_a|^2 - |\Psi(0)_e|^2) \quad [7]$$

In this equation, Z is the atomic number, e is the charge of an electron, R_E and R_G are the atomic radii for the excited and ground states, and $|\Psi(0)_a|^2$ and $|\Psi(0)_e|^2$ are the s-electron densities at the

nucleus of the absorbing and emitting nucleus, respectively. Small changes in the coordination environment for either source or absorber will lead to variations in the energy levels of the excited ($I_E = 3/2$) and ground states ($I_G = 1/2$) of the nuclei.

We summarize the isomer shifts for six iron complexes in Table II and relate the ORR half-wave potential to the isomer shift for these catalysts. A strong relationship can be observed from Table II and Fig. 3b: as the isomer shift increases, the catalytic activity is enhanced for these compounds, which can be assigned to a growing 3d electron density and a higher spin state for the iron atoms.⁷¹ Furthermore, the quadrupole splitting ΔE_Q in the Mössbauer spectroscopy of FeTAA, FePc, FeSalen and FeCorrole has also been listed in Table SIII, which is caused by an electric field gradient (EFG) at the iron nucleus and expresses the deviation from cubic symmetry.⁷⁰ It is generally related to the electron distribution in the orbitals and the local coordination environment.⁷² The observed quadrupole splitting values for FeTAA (0.72 m·ms⁻¹), FePc (0.69 m·ms⁻¹), and FeCorrole (0.76 m·ms⁻¹) mean the close deviation from symmetry caused by the similar Fe-N₄ coordination structure. However, the ΔE_Q value for FeSalen (0.89 m·ms⁻¹) is much larger than above three samples, which could be attributed to the increased electronegativity of O and the changes of Fe-O bond distance.

As reported above, the supporting ligands have a significant impact on the electron structure of the central Fe atom, which is considered as the active site in Fe complex catalysts. Therefore, the Fe site on six iron complexes was investigated to study the effect of ligand coordination on the ORR progress, as discussed below. The generally sluggish ORR kinetics is due to the high strength of the O-O bond and the requirement of an excellent catalyst to facilitate *OOH adsorption. The adsorption energies for *OOH are listed in Table III. The *OOH on FeTAA exhibits the strongest adsorption energy of -0.95 eV. For the FePc, the adsorption energy for *OOH is -0.66 eV, which is weaker by 0.29 eV compared to that on FeTAA. The adsorption energy of *OOH on FeSalen is -0.13 eV, which is the lowest. The stronger the bond formation between catalyst and OOH, the more powerful the catalyst will be in breaking the O-O bond; thus the catalytic activity levels should decrease in the sequence FeTAA > FePc > FeTPP > FeCorrole > FeTim > FeSalen.

The spin density and charge density, determining the adsorption strength between the active site and the adsorbates, can serve as the new activity descriptors of oxygen reduction. The structures of these molecules exhibit different charge and spin density distributions around the active site, which will influence the OOH adsorption and further O-O bond breakage. Based on these structures, Natural Population Analysis is used to investigate the charge distribution on

Table III. Calculated adsorption properties for OOH on various molecules.

	FeTAA	FePc	FeTPP	FeCorroles	FeTim	FeSalen
E _{ads} , OOH/eV	-0.95	-0.66	-0.53	-0.48	-0.32	-0.13
Charge on Fe site	1.565	0.712	0.690	0.377	0.337	0.342
Spin density (μ)	2.59	2.60	2.64	2.48	2.45	2.22

Figure 4. Room temperature Mössbauer absorption spectrum and its deconvolution for dry powders of iron complexes.

these molecules, as shown in Fig. 5. The spin density of the Fe atom is also shown in Table III. Accordingly,⁹ with a high spin effect and increasing positive charge effect, the binding energies for *OOH will be enhanced. In our study, the Fe atom in FeTAA, FePc and FeTPP with a higher spin density exhibits a higher adsorption energy for *OOH and better activity for the ORR. A medium spin density on FeCorrole and FeTim corresponds to a moderate *OOH adsorption energy and electrochemical performance, while FeSalen exhibits the lowest spin state and *OOH adsorption energy, resulting in the largest overpotential. For the charge distribution, the Fe site on all these molecules exhibits net positive charge. The charge sequence is found to be FeTAA > FePc > FeTPP > FeCorrole >

FeTim, which is consistent with the sequences for the *OOH adsorption energy and catalytic activity. One exception is FeSalen, which has a near charge density but a much lower spin density compared with FeTim. Therefore, a conclusion that increasing charge density and spin density could enhance the adsorption energy for *OOH can be drawn, which is consistent with the literature.⁹

Conclusions

In this paper, we prepared six iron complex compounds (FeTAA, FePc, FeTPP, FeSalen, FeCorrole, FeTim) and used them as catalysts to study the ORR using cyclic voltammetry and rotating

Figure 5. The charge and spin analysis graphics for various molecules: (a) FeCorrole, (b) FePc, (c) FeSalen, (d) FeTAA, (e) FeTim and (f) FeTPP. The pink values on the balls represent the value of the charge determined using Natural Population Analysis and the red values represent the spin density of the Fe atom. The purple, blue, green, grey and white balls represent the Fe, N, Cl, C, H atoms, respectively.

disk electrode methods in acidic media. We found that even with the same metal species, the ORR performance for these complexes exhibited prominent differences in terms of reaction activity, product and mechanism. The electrochemical activity was found to follow the sequence of FeTAA > FePc > FeTPP > FeCorrole > FeTim > FeSalen. An electron-transfer number close to 4 was derived for FeTAA, FePc, FeTPP and FeCorrole, demonstrating a complete reduction of oxygen to H₂O, while an incomplete reduction to peroxide was implied in the ORR catalysed by FeTim and FeSalen. Different Tafel slopes indicated changed ORR rate determining steps and reaction mechanisms.

Furthermore, the electron-structure of the iron complexes regulated by the surrounding ligands was investigated by oxidation-state sensitive XANES and spin-state sensitive Mössbauer spectroscopy. The Fe components with a higher oxidant state and a tetrahedral coordination structure, as revealed by a positive shift of position and higher intensity of the pre-edge peak in the XANES spectra, respectively, proved to be more active in the ORR process. The relationship of enhanced catalytic activity for these compounds with increasing isomer shift in Mössbauer spectroscopy was identified, which can be assigned to a growing 3d electron density and a higher spin state in the iron atoms. Density function theory (DFT) calculations were carried out to verify these conclusions: the charge density and spin density in Fe centres regulated by coordination effects can be regarded as the two factors that increase the adsorption strength between the active site and *OOH species and promote O–O bond breakage and the basic design strategy with a metal centre of higher charge density and spin density by tuning coordination sphere should be developed.

Acknowledgments

Q.H. acknowledges the financial support from the National Natural Science Foundation of China (grant nos. 21978260, 21676241, and U1732111). We also thank Dr. Yongfeng Hu for the help with the analysis of XAS data.

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