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Article

Redox chemistry of N_4 - Fe^{2+} in iron phthalocyanines for oxygen reduction reaction

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ABSTRACT

A precise understanding of the redox chemistry of N_m - M^{n+} (like N_4 - Fe^{2+}) systems is essential for fundamental studies and rational design of N_m - M^{n+} -based electrocatalysts for the oxygen reduction reaction (ORR). Herein, three different iron phthalocyanines (FePcs) adsorbed on carbon nanotubes ($(NH_2)_4FePc@CNTs$, $(t-Bu)_4FePc@CNTs$, and $FePc@CNTs$) were evaluated to demonstrate the effect of the electron donating power of the substituents on the Fe^{3+}/Fe^{2+} redox potential of $FePc@CNTs$ and the role of these composites as ORR mediators in alkaline media. The Fe^{3+}/Fe^{2+} redox potential of the FePcs was found to shift towards the cathodic region upon substitution with electron-donating groups. This up-field shift in the e_g -orbital leads to a lower overlap between the onset potential of the Fe^{3+}/Fe^{2+} redox couple and that of the ORR, and thus, the ORR activity decreased in the following order based on the substitution of FePc: $-H > -t-Bu > -NH_2$.

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1. Introduction

The redox chemistry of MN_4 -macrocycles is highly conducive to their use as electrocatalysts for reactions involving H_2 , O_2 , and CO_2 [1–4]. These reactions are in high demand for development of the energy sector. The oxygen reduction reaction (ORR) at the cathode surface is of particular interest, where the poor kinetics of the ORR is among the serious issues that constrain the industrial use of fuel cell devices [5]. Platinum is a good catalyst for the ORR, but its high cost limits its further use.

Therefore, new strategies in this field have become important for addressing the scientific and technological issues of decreasing the use of Pt and advancing the development of non-Pt electrocatalysts [6].

A number of MN_4 -macrocyclic complexes, such as metallo-porphyrins, metallo-corroles, and metallo-phthalocyanines were found to have good ORR performance [7]. Iron phthalocyanine (FePc) has been widely studied because of its planar and fully conjugated structure and redox rich chemistry, where the latter facilitates the ORR on the active site (N_4 - Fe^{2+}), fol-

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lowed by e^- transfer via the inner-sphere mechanism [8,9]. The ORR activity MN_4 -complexes strongly depends on the environment of the MN_4 moiety, which determines the redox potential of the metal ion (a primary ORR activity descriptor) [10]. The distinction in the ORR activity and kinetics of MN_4 -macrocycles in basic versus acidic environments can be ascribed to the shift in the redox potential of the central metal ion with the pH and reaction intermediates (H_2O_2 vs. HO_2^-). Generally, FePc forms two redox couples: Fe^{2+}/Fe^+ and Fe^{3+}/Fe^{2+} in both acidic and basic media. The Fe^{3+}/Fe^{2+} redox couple is formed at more positive potential, whereas the redox transition at lower positive potential is ascribed to Fe^{2+}/Fe^+ [11–13]. Chemical modification of the FePc framework is a very useful strategy for altering the redox potential of the Fe metal ions, resulting in variation in the ORR activity of FePc. This strategy opens the door for the development of novel MN_4 -based electrocatalysts with improved catalytic performance [14,15]. The electron-withdrawing groups can shift the potential of the Fe^{3+}/Fe^{2+} redox couple in the anodic direction and vice versa for electron-donating groups [16]. An increasingly negative formal potential (easier to oxidize the metal center) or progressively positive formal potential (more difficult to oxidize the metal center) of the Fe^{3+}/Fe^{2+} redox couple does not permit the best possible ORR catalysis at the cathode. Accordingly, the Fe^{3+}/Fe^{2+} redox potential should be situated in an appropriate potential window to achieve higher ORR activity. Optimum electronic coupling of the highest occupied molecular orbital (HOMO) of the metal ion (represented by the M^{3+}/M^{2+} redox couple potential or e_g -orbital energy) with the lowest unoccupied molecular orbital (LUMO) of the dioxygen molecule results in significant ORR activity, which is also supported by perturbation theory [17]. Besides, several published reports suggest a relationship between the ORR activity and potential of the M^{3+}/M^{2+} redox couple in metallo-phthalocyanines, indicating an enhancement of the ORR activity of metallo-phthalocyanines with the anodic shift in the formal potential of the central metal ion. However, it is still unclear whether the potential of the M^{3+}/M^{2+} redox couple should be close or equal to the ORR onset potential for maximizing the ORR activity [18,14].

Herein, we extend this work by studying the effect of electron-donating substituents (especially the $-NH_2$ group, which has not been reported in the redox potential vs. formal potential volcano plot for FePcs) on the Fe^{2+}/Fe^{3+} redox potential and ORR activity of FePc with three different substituents ($FePc(NH_2)_4$, $FePc(t-Bu)_4$, and FePc, respectively) adsorbed on carbon nanotubes (CNTs) by using a microwave method. CNTs were selected as a carbon support because of the instability of FePcs catalysts on the electrode surface without a support. The composites were synthesized under microwave irradiation by controlling the reaction parameters and energy efficiency. Relatively low-energy microwave radiation prevents destruction of the chemical bonds in the FePc macrocyclic frameworks and provides a good distribution of FePc on the CNT surface, with high crystallinity. After fabricating the composites, we methodically probe the electrochemistry of the $(NH_2)_4FePc@CNTs$, $(t-Bu)_4FePc@CNTs$, and $FePc@CNTs$, and demonstrate that

electron-donating substituents detrimentally affect the ORR electrocatalytic activity of FePc. Specifically, the $FePc@CNTs$ are found to be the best ORR catalyst of those evaluated. Further, scientific depictions are presented to provide a basic understanding of the ORR on MN_4 -macrocyclic catalysts.

2. Experimental

2.1. Chemicals and materials

MWCNTs, FePc (Sigma Aldrich), $(t-Bu)_4FePc$ (Sigma Aldrich), $(NH_2)_4FePc$ (Sigma Aldrich), and solvents such as ethanol, methanol, xylene, and Nafion solution (0.5 wt% in alcohol) were utilized as received from the manufacturer.

2.2. Functionalization of multiwall carbon nanotubes

In a typical experiment, 0.5 g of multiwall carbon nanotubes (MWCNTs) was transferred to a 100 mL beaker containing 10 mL of conc. HNO_3 and 30 mL H_2SO_4 , and kept for 30 min under ultrasonic treatment. The resulting black slurry was heated at 140 °C for 2 h with constant stirring, washed with deionized water several times until neutral pH was achieved, and finally dried at 60 °C overnight.

2.3. Catalyst preparation

FePc (50 mg) and the functionalized carbon nanotubes (150 mg) were added to 10 mL ethanol with ultrasonic treatment. The observed slurry was transferred into a microwave autoclave containing 5 mL xylene, and irradiated at 350 W and 150 °C for 30 min. The obtained black precipitates were collected by centrifugation at 5000 rpm, washed successively with ethanol, and dried at 60 °C overnight. The obtained solid powders are denoted as $FePc@CNTs$. The remaining composites, $FePc(t-Bu)_4@CNTs$ and $FePc(NH_2)_4@CNTs$, were also prepared by a similar method.

2.4. Characterization

Fourier transform-infrared (FT-IR) and ultraviolet-visible (UV-vis) spectra were recorded with a Nicolet 730 FT-IR Spectrometer and Perkin Elmer Lambda 900 instrument, respectively. The morphologies of all samples were analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) using a Zeiss SUPRA 55 and FEI Tecnai G2 20 instrument, respectively. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were carried out with a Shimadzu XRD-6000 ($Cu K\alpha$ radiation (40 kV, 30 mA, $\lambda = 1.5418 \text{ \AA}$)) and a PHI Quantera II XPS scanning microprobe, respectively.

2.5. Catalyst ink preparation and electrochemical measurements

The catalyst ink containing the $FePcs@CNTs$ was prepared by adding 15 mg of $FePcs@CNTs$ and 10 μL of 0.5 wt% Nafion

to 1 mL ethanol, followed by sonication for 15 min. Similarly, 20% Pt/C ink was also prepared by mixing 15 mg of 20 wt% Pt/C in 1 mL ethanol. Thereafter, 1.8 μL FePcs@CNT or Pt/C catalyst ink was dropped onto the working electrode (the resulting catalyst loading was 0.25 $\mu\text{g}/\text{cm}^2$) for the electrochemical investigations.

Rotating disc electrode (RDE) investigations were carried out on a multi-potentiostat (Bio-Logic SP150) and RDE Pine instrument. An electrocatalytic cell was constructed by using a working electrode (glassy carbon, 5 mm diameter), Ag/AgCl, reference electrode (3 M KCl), and a carbon counter electrode. For the electrode pretreatment, the working electrode was cleaned mechanically with alumina slurry. After obtaining a mirror-finish on the electrode surface, the electrode was washed initially with Milli-Q water and acetone, and dried.

All measurements were performed in the potential range of 0 to -1.0 V vs. Ag/AgCl. Linear sweep voltammograms (LSVs) were recorded at a scan rate of 50 mV/s with a 1600 rpm electrode rotation rate. Oxygen was passed directly into the cell for approximately 30 min before the test.

The measured potentials were converted to the reversible hydrogen electrode (RHE) scale using Eq. (1):

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + E^0_{\text{Ag/AgCl}} \quad (1)$$

where E_{RHE} is the potential vs. RHE, $E_{\text{Ag/AgCl}}$ is the experimental potential vs. Ag/AgCl, and $E^0_{\text{Ag/AgCl}}$ is the standard potential of Ag/AgCl (0.210 V) at 25 $^{\circ}\text{C}$.

The Koutecky-Levich Eqs. (2) and (3) were used to calculate the number of electrons transferred (n) per oxygen molecule and the kinetic limiting current density (j_k).

$$\frac{1}{j} = \frac{1}{j_L} + \frac{1}{j_k} = \frac{1}{B\omega^{1/2}} + \frac{1}{j_k} \quad (2)$$

$$B = 0.62nFCD_0^{2/3}\nu^{-1/6} \quad (3)$$

where j is the measured current density, j_k is the kinetic current density, j_L is the diffusion limiting current density, ω is the angular velocity of the disk ($2\pi N$, where N is the linear rotation speed), n is the number of electrons transferred in the ORR, F is the Faraday constant ($F = 96485$ C/mol), C_0 is the bulk concentration of O_2 , ν is the electrolyte viscosity, $C_0 = 1.2 \times 10^{-3}$ mol/L, $D_0 = 1.9 \times 10^{-5}$ cm/s, and $\nu = 0.1$ v/s in 0.1 M KOH.

3. Results and discussion

3.1. Characterization of the composites

The FePc@CNTs, $(t\text{-Bu})_4\text{FePc@CNTs}$, and $(\text{NH}_2)_4\text{FePc@CNTs}$ were synthesized via a microwave-assisted method (see Section 2.3), as illustrated in Scheme 1. The structures of the FePcs used herein are shown in Fig. S1.

The typical TEM images of the CNTs show a smooth surface (Figs. 1(a,b)) without any holes or adsorbed molecular species (such as FePcs). However, the TEM images of the FePc@CNTs (Figs. 1(c,d)) indicate adsorption of the FePc crystals on the surface of the CNTs, with high crystallinity [20]. The SEM image (Fig. S2(c)) of the FePc@CNTs shows distinct aggregation of the FePcs adsorbed on the CNTs. These results indicate that microwave irradiation induced adsorption of the FePc molecules

Scheme 1. Schematic representation of synthesis of FePc@CNTs composite via microwave-assisted strategy.

on the CNT surface via π - π stacking interaction.

Various spectroscopic techniques were used to probe the structural features of the composites. FT-IR study was applied to provide evidence of incorporation of the FePcs in the composites. The FT-IR spectra of the FePcs@CNTs show peaks of the FePc framework at 750–755, 1165–1180, and 1325–1330 cm^{-1} , while the other peaks at 1220–1270, 1540–1560, and 1725–1728 cm^{-1} respectively correspond to the C–O–C, C=C, and C=O vibrations of the CNTs (Fig. 2(a)) [19]. The FT-IR spectra of the $(t\text{-Bu})_4\text{FePc@CNTs}$ and $(\text{NH}_2)_4\text{FePc@CNTs}$ show strong peaks at 2958 and 3419–3468 cm^{-1} due to the t -butyl groups and free $-\text{NH}_2$ groups, respectively. These results indicate that the structure of the FePcs on the CNT surface was preserved (in the FePcs@CNT composites) without any change in the functional groups of the FePcs, as supported by the FT-IR spectra of pure FePcs (Fig. S2(a)).

UV-vis studies in ethanol (Fig. 2(b)) confirmed the effect of

Fig. 1. TEM images of CNTs (a) and enlarged view of selected CNTs (b), FePc@CNTs (c) and enlarged view of selected FePc@CNTs (d).

Fig. 2. (a) FT-IR spectra of CNTs and FePcs@CNTs; (b) UV-visible spectra of CNTs, unsupported FePcs, and FePcs@CNTs; (c) XRD pattern of FePcs@CNTs; (d) Expanded view of XRD pattern of (t-Bu)₄FePc@CNTs.

the substituents on the energy levels of the unsupported FePcs and the interaction between the FePcs and CNTs in the FePcs@CNT composites. The UV-vis spectra of the unsupported FePcs show two absorption bands assigned as the Soret and Q bands, which can be assigned to the LUMO at high energy and HOMO at low energy, respectively. The UV-vis spectra of unsupported FePc, (t-Bu)₄FePc, and (NH₂)₄FePc demonstrated extended wavelength shifts of the Q band by 12 nm for FePc vs. (t-Bu)₄FePc and 30 nm for (t-Bu)₄FePc vs. (NH₂)₄FePc, indicating an upshift in the HOMO energy level (dz²-orbital) of the FePcs with introduction of the electron donating substituents, as previously reported for FePc and FePc(t-Bu)₄ [18]. Furthermore, the observed Soret bands at 323.0, 324.1, and 352.0 nm are related to metal-to-ligand charge transfer in FePc, (t-Bu)₄FePc, and (NH₂)₄FePc, respectively. Further, the UV-vis spectra of the FePcs@CNT composites showed Q bands at a position similar to that of the unsupported FePcs, suggesting that the HOMO energy levels of the composites are similar to those of the corresponding unsupported FePcs. The UV-vis spectra of the FePcs@CNTs show a shift of the Soret band to higher energy, plausibly due to an increase in the LUMO energy of the FePcs@CNT composites [18]. Thus, the observed upfield shift in the dz²-orbital of the FePcs@CNTs can be attributed predominantly to the electron-donating substituents.

The XRD patterns of the unsupported FePcs (Fig. S2(b)) show a sharp diffraction peak at ca. 7°–20°. The peaks in XRD

pattern of the FePcs@CNT composites were also similar to those of the unsupported FePcs, indicating aggregation of the FePcs on the surface of the CNTs (Figs. 2(c,d)). However, the newly observed broad diffraction peak at ca. 25° for each composite can be attributed to the CNTs.

The N 1s XPS spectra (Fig. S3(a)) display two signals at 399.70 and 400.10 eV, confirming the presence of C–N and C=N nitrogen in the composite, respectively. The Fe 2p scan (Fig. S3(b)) shows peaks at 709.5, 711.8, and 717.2 eV, corresponding to the 2p_{3/2} (Fe²⁺) and 2p_{3/2} (Fe³⁺) states of Fe–O (due to oxygen aggregates formed after functionalization with the CNTs, and species formed by columbic forces between the FePcs and CNT surface), respectively, while the satellites peaks at 723.5 and 725.3 eV are due to the 2p_{1/2} (Fe²⁺) and 2p_{1/2} (Fe³⁺) species, respectively [19]. Similarly, the N 1s and Fe 2p XPS profiles of the other composites (t-Bu)₄FePc@CNTs and (NH₂)₄FePc@CNTs were also obtained (Figs. S3(a,b)). The C 1s XPS scans and XPS survey spectrum are in good agreement with the carbon-containing functional groups and the elemental structure of each sample, respectively (Fig. S4(a)).

Raman studies (Fig. S4(b)) showed a considerable increase in the I_D/I_G ratio for the FePc@CNT composite as compared to that of the CNTs, demonstrating the creation of some defects on the CNT surface in the former. Thus, characterization of the unsupported FePcs and FePcs@CNTs using the aforementioned multiple spectroscopic techniques confirmed the incorporation

of FePcs on the surface of the CNTs without affecting the structural features. The next section presents electrochemical characterization of the composite and its use in electrocatalysis of the ORR.

3.2. Electrochemistry of FePcs@CNTs in 0.1 M KOH under N_2/O_2 atmosphere

The electrode for the electrochemical measurements was prepared as described in Section 2.6. For all samples, cyclic voltammograms (CVs) were recorded in 0.1 M KOH under N_2 . The CVs of the FePc@CNTs, $(t\text{-Bu})_4\text{FePc@CNTs}$, and $(\text{NH}_2)_4\text{FePc@CNTs}$ exhibit peaks of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple at 0.841 V, 0.503 V, and 0.555 V, respectively (dashed line in Fig. 3(a)). Additionally, the CV of the FePc@CNTs shows a peak of another redox couple at 0.290 V, which may be due to the $\text{Fe}^{2+}/\text{Fe}^+$ transition. However, such redox couples were absent in the CVs of the functionalized CNTs (Fig. S5(b)). These results confirm that these redox couples originate from the FePcs, where the driving force for stabilizing the FePcs on the CNT surface is the π - π stacking force.

The observed variations in the redox potentials of the

$\text{Fe}^{3+}/\text{Fe}^{2+}$ couple of the FePcs can be assigned to the substituent effect. It was pointed out that electron-donating substituents shifted the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox potential towards the cathodic region, as compared to $-\text{H}$ in the unsubstituted FePcs.

For the FePc@CNT composite, the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox process was found to be reversible with a 60 mV peak separation. Further, the CVs of the FePc@CNTs were likewise recorded at various sweep rates of 20–100 mV/s under similar experimental conditions (Fig. S6(a)) and the anodic and cathodic peaks followed the Randles-Sevcik equation (Eq. (4)) (Fig. S6(b)) [21].

$$i_p = \alpha v^{1/2} \quad (4)$$

Here, i_p is the peak current (in μA) and v is the scan rate (in mVs^{-1}).

Further, the CVs of the FePc@CNT, $(t\text{-Bu})_4\text{FePc@CNT}$, and $(\text{NH}_2)_4\text{FePc@CNT}$ composites (solid line CVs in Fig. 3(a)) and CNTs (Fig. S5(b)) were recorded with 0.1 M KOH under O_2 . The results show a relationship between the potential of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple and ORR activity for all FePcs@CNTs. However, the FePc@CNTs were more effective for catalyzing the ORR than the $(t\text{-Bu})_4\text{FePc@CNTs}$, $(\text{NH}_2)_4\text{FePc@CNTs}$, and CNTs. This may be due to the proximity of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox potential to the ORR potential of the FePc@CNTs as compared

Fig. 3. (a) CVs of $(\text{NH}_2)_4\text{FePc@CNTs}$, $(t\text{-Bu})_4\text{FePc@CNTs}$, and FePc@CNTs recorded in 0.1 M KOH under O_2/N_2 environment at 50 mV s^{-1} scan rate; (b) LSV curves for FePc@CNTs, $(\text{NH}_2)_4\text{FePc@CNTs}$, $(t\text{-Bu})_4\text{FePc@CNTs}$, and 20% Pt/C, recorded in 0.1 M KOH in presence of O_2 at 5 mV s^{-1} with 1600 rpm rotation rate; (c) Comparison of ORR activity in terms of $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox potential vs. ORR formal potential; (d) LSV curves of FePc@CNTs before and after dipping in thiocyanate anion (SCN^-) at 5 mV s^{-1} scan rate with 1600 r/min rotation rate.

to that of the $(t\text{-Bu})_4\text{FePc@CNTs}$ and $(\text{NH}_2)_4\text{FePc@CNTs}$. Because the electron-donating substituents caused a cathodic shift in the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox potential in the order of $(\text{NH}_2)_4\text{FePc@CNTs} > (t\text{-Bu})_4\text{FePc@CNTs} > \text{FePc@CNTs}$, the ORR electrocatalytic activity followed the order: $(\text{NH}_2)_4\text{FePc@CNTs} < (t\text{-Bu})_4\text{FePc@CNTs} < \text{FePc@CNTs}$.

3.3. ORR kinetics and e^- transfer mechanism

The ORR kinetics of the composite FePc@CNTs were investigated by employing LSV. Fig. 3(b) shows the polarization curves of the FePc@CNTs , $(t\text{-Bu})_4\text{FePc@CNTs}$, $(\text{NH}_2)_4\text{FePc@CNTs}$, and traditional catalyst 20% Pt/C. The ORR onset potential of the FePc@CNTs , $(t\text{-Bu})_4\text{FePc@CNTs}$, and $(\text{NH}_2)_4\text{FePc@CNTs}$ was 0.98 V, 0.96 V, and 0.96 V, respectively, whereas the formal potential ($E_{1/2}$) for these composites followed the trend: $(\text{NH}_2)_4\text{FePc@CNTs}$ (0.83 V) < $(t\text{-Bu})_4\text{FePc@CNTs}$ (0.87 V) < FePc@CNTs (0.91 V). Consequently, the FePc@CNTs exhibited a more positive $E_{1/2}$ than the 20% Pt/C catalyst (0.85 V), indicating the excellent ORR performance of the former.

The plot (Fig. 3(c)) of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox potential vs. the ORR formal potential measured from the CVs and LSVs of the FePcs@CNTs suggests that the electron-donating group had a detrimental effect on the electrocatalytic activity of FePc for the ORR by pushing the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox potential into the cathodic region. These outcomes indicate that the potential of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple must be located near the ORR potential window to achieve significant ORR activity.

Figs. S7(a,b) respectively display the LSV curves recorded at various scan rates and the Koutecky-Levich plots at numerous electrode potentials for the FePc@CNT composite. The slopes were found to be parallel to one another, accompanied by first-order kinetic behavior and a similar number of electron exchanges at various potentials during the ORR. The slopes of the $1/J$ vs. $\omega^{-1/2}$ plots indicate the involvement of 3.82 electrons in O_2 electrocatalysis (see Supporting Information). Therefore, analysis of the onset potential (0.98 vs. RHE) and transferred electrons ($n = 3.82$) indicates that the FePc@CNTs show better catalytic activity than 20% Pt/C. Further, the methanol tolerance of the FePc@CNT composite was investigated by recording the CV and LSV curves in a mixed electrolyte (25 mL of 0.1 M KOH and 5 mL of CH_3OH) in the presence of O_2 . The outcomes demonstrated modest fluctuations (Figs. S8(a,b)) in the catalyst performance in the presence of methanol. The stability of the FePc@CNT composite was also evaluated by recording the CVs and LSVs after 4000 CV cycles using 0.1 M KOH in the presence of O_2 (Figs. S9(a,b)). The FePc@CNT composite exhibited remarkable stability, showing a 27 mV negative shift toward the ORR half-wave potential and 1 mA/cm^2 decay in the current density.

Further, SCN^- was used to investigate the ORR inhibiting effect and to demonstrate the real active sites in the FePc@CNT composites, where the FePc@CNT electrode was submerged in a mixed electrolyte (5 mL of 5 mM KSCN and 25 mL of 0.1 M KOH) for 1 h. The CVs (Fig. S10(a)) and LSVs (Fig. 3(d) for FePc@CNTs and Fig. S10(b–c) for 20% Pt/C) of the corresponding electrodes were recorded with and without exposure

in the above-mentioned mixed electrolyte. The findings suggest that the $E_{1/2}$ of the FePc@CNTs declined by 150 mV (165 mV with 20% Pt/C) and the current density fell by 88.13% (76.27% loss for 20% Pt/C) in the presence of SCN^- . These observations indicate that SCN^- poisoning decreased the availability of ORR active sites for further ORR (Eqs. (8) and (9)) [9].

The $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple of the FePc@CNTs is responsible for O_2 electrocatalysis, where $\text{N}_4\text{-Fe}^{2+}$ is an active site for the ORR [22,23], as supported by the extreme sensitivity of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple toward O_2 . Thus, the ORR kinetics of the composite FePc@CNTs with 0.1 M KOH in O_2 environment showed that O_2 could easily replace the OH^- from the active sites and was reduced via $4e^-$ ORR (similar to the role of SCN^- during the ORR) (Eqs. (5)–(7)) [24–26].

ORR Mechanism:

SCN⁻ Effect:

3.4. Electrochemistry of FePcs@CNTs in 0.1 M H_2SO_4 in presence of O_2

The CVs of the FePcs@CNTs were acquired in N_2 -sparged 0.1 M H_2SO_4 at 50 mV s^{-1} scan rate (see inset of Figs. S11(a–c)). Under these trial conditions, no $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox peak was observed for the $(\text{NH}_2)_4\text{FePc@CNTs}$, whereas the FePc@CNTs and $(t\text{-Bu})_4\text{FePc@CNTs}$ composites underwent the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox process at 0.56 V and 0.55 V, respectively [27]. The $(t\text{-Bu})_4\text{FePc@CNTs}$ also showed signals of another redox couple at +0.18 V, which can be ascribed to the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox process. Further, the CVs of the FePcs@CNTs were recorded with 0.1 M H_2SO_4 in the presence of O_2 at 50 mV s^{-1} scan rate (Figs. S11(a–c)).

By comparison with the CVs acquired under N_2 , it is deduced that a synergistic reaction occurs in the presence of O_2 , except in the case of the $(\text{NH}_2)_4\text{FePc@CNTs}$, whereby the ORR activity in alkaline media follows the same trend as the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox process. The ORR activity of metal phthalocyanine catalysts is notoriously lost in acidic media [28,29]. Similarly, the LSV curves (Fig. S10(d)) recorded using 0.1 M H_2SO_4 in the presence of O_2 at 5 mV s^{-1} scan rate suggest that the FePcs@CNTs catalyst showed poor stability in O_2 -sparged 0.1 M H_2SO_4 electrolyte, where the loss of activity followed the order: $\text{FePc@CNTs} > (t\text{-Bu})_4\text{FePc@CNTs} > (\text{NH}_2)_4\text{FePc@CNTs}$. This decline in the ORR activity may be ascribed to disruption of the phthalocyanine structure or demetallation of iron from the phthalocyanine system because of hydrogenation of the ligating C=N group. Furthermore, the $(\text{NH}_2)_4\text{FePc@CNTs}$ showed extra sensitivity in acidic medium, possibly due to protonation of the $-\text{NH}_2$ groups.

Finally, the observed differences in the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox potential with substitution of FePc and the impact of the substituents on the ORR in basic/acidic media can be attributed to the following significant features: (1) the relative energy difference

Fig. 4. Representation of up-shift in the e_g -orbital with strongly electron donating groups (relative hardness of Fe- O_2 adduct).

of the dz^2 orbital (e_g -orbital) of the N_4 - Fe^{2+} center vs. the Fermi levels, (2) the energy gap between the HOMO (dz^2 orbital or redox potential) of the N_4 - Fe^{2+} center and LUMO (π^* orbital or ORR onset potential) of dioxygen, and (3) the C-support as a component of the e^- donor/acceptor species. The peripheral substituents on the FePc structure balance the e^- density on the N_4 - Fe^{2+} active site, which influences the ORR electrocatalysis. The e^- -donating substituents provide a higher electron density at the N_4 - Fe^{2+} active site. This results in higher the donor-acceptor intermolecular hardness (η_{DA}) (HOMO-LUMO energy gap or possibly the gap between the onset potentials of the Fe^{2+}/Fe^{3+} redox reaction and ORR), accompanied by an up-shift in the e_g -orbital, especially in the dz^2 -orbital of the Fe ion (i.e., a relatively harder N_4 - $Fe^{2+}-O_2$ adduct) [30–32]. These factors can also enhance bonding of the ORR intermediates with the N_4 - Fe^{2+} active site and thus reduce the effectiveness of the ORR. These assertions are in good agreement with the shift of the Q-band to the longer wavelength region of the UV-vis spectrum with the substituents having higher electron donating power. Fig. 4 shows a systematic representation of the up-shift in the e_g -orbital with strongly electron donating groups and the formation of the corresponding N_4 - $Fe^{2+}-O_2$ adduct.

4. Conclusions

Electrochemical studies were performed to achieve fundamental understanding of the ORR on molecular electrocatalysts at the molecular-level. The effect of the Fe^{2+}/Fe^{3+} redox potential during ORR electrocatalysis using FePc, $(t-Bu)_4$ FePc, and $(NH_2)_4$ FePc was investigated in alkaline media. We demonstrated that electron-donating groups on FePc can significantly modify the electron density at the N_4 - Fe^{2+} active site, increasing the energy of the dz^2 -orbital (HOMO), and inducing a significant shift of the Fe^{2+}/Fe^{3+} redox potential in the cathodic direction. Therefore, the interaction between the HOMO of the N_4 - Fe^{2+} active site and LUMO of O_2 decreased with strongly electron donating substituents, leading to a lower ORR. Thus, electron donating groups on the periphery of the FePc framework are

not favorable for the ORR. In comparison with other composites and 20% Pt/C, the FePc@CNT composite displayed higher performance in terms of the ORR activity, methanol tolerance, and durability. Under SCN^- poisoning, formation of the Fe^{3+} state could be anticipated in the Fe^{2+}/Fe^{3+} redox process, decreasing the availability of ORR active sites.

Electronic supporting information

Supporting information is available in the online version of this article.

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Graphical Abstract

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Redox chemistry of N_4 - Fe^{2+} in iron phthalocyanines for oxygen reduction reaction

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Electron-donating groups on FePc increase the energy gap between the HOMO (dz^2 orbital or Fe^{2+}/Fe^{3+} redox potential) of the N_4 - Fe^{2+} center and LUMO (π^* orbital or ORR onset potential) of dioxygen.

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摘要: 准确理解金属大环配合物(如 N_4 - Fe^{2+})体系的氧化还原化学性能, 对氧还原反应(ORR)电催化剂的基础研究和合理设计具有重要意义。本文采用微波法将三种不同酞菁铁类金属大环配合物吸附在碳纳米管上, 分别记为 $(NH_2)_4FePc@CNTs$, $(t-Bu)_4FePc@CNTs$ 和 $FePc@CNTs$, 考察了取代基对 Fe^{3+}/Fe^{2+} 氧化还原电位的影响, 以及碱性介质中的氧还原反应催化活性。结果表明, $FePc@CNTs$, $(t-Bu)_4FePc@CNTs$ 和 $(NH_2)_4FePc@CNTs$ 的ORR起始电位分别为0.98, 0.96和0.96 V, 而半波电位($E_{1/2}$)由高到低的顺序为 $FePc@CNTs$ ($E_{1/2} = 0.91$ V), $(t-Bu)_4FePc@CNTs$ ($E_{1/2} = 0.87$ V), $(NH_2)_4FePc@CNTs$ ($E_{1/2} = 0.83$ V)。与20% Pt/C ($E_{1/2} = 0.85$ V)相比, $FePc@CNTs$ 和 $(t-Bu)_4FePc@CNTs$ 具有优异的ORR性能。在活性、稳定性和耐甲醇性方面, $FePc@CNTs$ 复合材料比其他复合材料表现出更高的ORR性能。

研究发现, FePc上的供电子基团可以显著改变 N_4 -Fe²⁺活性位点的电子云密度, 增加 d_z^2 轨道(HOMO)的能量, 并观察到Fe²⁺/Fe³⁺氧化还原电位显著向阴极方向移动. 结果表明, 取代基的高电子贡献能力降低了HOMO和LUMO(O_2 的杂轨道*-轨道)之间的电子耦合, 从而降低了氧还原催化活性. 因此, FePc框架外围的供电子基团对ORR不利.

本文阐明了取代基电子效应-金属大环配合物氧化还原电位与ORR催化性能之间的关系, 为ORR催化剂活性中心的构建和调控提供了借鉴.

关键词: 酞菁铁; 取代效应; 氧还原反应; 碳纳米管; 活性描述符

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