Journal of Materials Chemistry A



View Article Online

COMMUNICATION

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Cite this: DOI: 10.1039/c7ta02381b

Received 17th March 2017 Accepted 15th May 2017

DOI: 10.1039/c7ta02381b

rsc.li/materials-a

Biomimetic reduction of O₂ in an acid medium on iron phthalocyanines axially coordinated to pyridine anchored on carbon nanotubes

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An efficient and inexpensive catalyst for the oxygen reduction reaction (ORR) is the key missing component for large-scale development of fuel cells. Bio-inspired tethered electrocatalysts could be the solution to this problematic reaction. Either unsubstituted Fe phthalocvanine (FePc) or Fe hexadecachloro-phthalocyanine (16(Cl)FePc) was anchored to carbon nanotubes (CNTs) via a pyridine axial ligand. The results show that the fifth coordination plays a major role in increasing the catalytic activity of FePc and 16(Cl)FePc for the ORR. The coordination also allows the decoupling of the metal centre from the carbon support, thus changing the geometrical and electronic structure and hindering the production of H2O2. The pentacoordinated catalysts were stable in acidic pH according to the rotating disk analysis, but the activity of the hexadecachloro compound was not higher than that of the unsubstituted phthalocyanine. Cl atoms reduced the coupling between O₂ and Fe, mismatching the energy of the frontier orbitals and lowering the activity towards the reduction of O₂.

Introduction

The oxygen reduction reaction (ORR) is an important process in fuel cells, but its sluggish kinetics gives rise to a high overpotential in the cathode, which causes a voltage loss of the cell under operating conditions. This problem is partially solved by using very costly Pt-based catalysts in the O_2 cathode. A class of catalysts known as "non-precious metal catalysts" (NPMC), have been developed to substitute Pt used in the cathode of fuel cells. Metal-phthalocyanines and metal-porphyrins *i.e.* moieties containing a metal (*e.g.* Fe or Co) and four pyrrolic nitrogen atoms (MN₄) belong to this class of catalysts. The role of MN₄ as

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a catalyst in the ORR¹⁻⁴ and other reactions⁵⁻⁸ has been investigated for several years as reviewed in the references,1 but little progress has been made in improving major drawbacks such as an activity lower than Pt and poor stability in the presence of fuel cell electrolytes, especially in acidic environments.4,9-12 In an attempt to overcome these drawbacks, the following strategies have been adopted: (i) the synthesis of complexes with more positive redox potentials;¹³⁻¹⁵ (ii) the pyrolysis of the MN₄ complexes with different carbon supports;16-19 and (iii) the support of MN₄ complexes on different carbon nanostructures with or without coordination of a fifth ligand.²⁰⁻²⁶ Already in the 70's, Randin¹³ and Beck¹⁴ had proposed that the activity of MN₄ catalysts could be related to the M(m)/(n) redox potential, but rather few authors developed this concept any further.⁴ Volcano correlations have then been obtained in which the activity is correlated with the formal redox potential of MN₄.^{15,27-29} The heat treatment modifies the ligand structure around the metal, thereby making it more electron-withdrawing, and shifts the M(III)/(II) redox potential in the positive direction. This partially explains the higher activity of these materials,30 which can compete with Pt-based catalysts.^{3,31} Unfortunately, the structural changes are still unpredictable and therefore difficult to rationalize.30,32,33 On the other hand, electrocatalysts with increased activity and stability²¹⁻²⁴ have been produced through the synthesis of new penta-coordinated catalysts whose structures mimic the structures that exist in nature, such as the active site of the cytochrome c oxidase and haemoglobin.

In this communication, we analyse the catalytic activity of unsubstituted Fe phthalocyanine (FePc) and of Fe hexadecachloro-phthalocyanine (16(Cl)FePc) for the reduction of O₂ in acid, in the absence and in the presence of a pyridine axial ligand attached to the external walls of the CNTs. FeN₄ moieties were either absorbed directly onto the CNT by π interactions (CNT-FeN₄) or coordinated to pyridine axial ligands previously attached to the CNT by diazonium salt modification (CNT-Py-FeN₄). Among the MN₄ catalysts, Fe-based MN₄ are the most promising due to their high activity and the fact that they promote the direct ORR to water, *i.e.* bypassing the production

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of H_2O_2 in alkaline media. 16(Cl)FePc is known for the high redox potential of the Fe redox centre which stems from the electron-withdrawing effect of the Cl atoms present on the phthalocyanine ring,^{1,15,34} and presents higher activity than unsubstituted FePc.¹ While the activity of FePc anchored on CNTs *via* an axial ligand has been reported,²⁰⁻²⁴ little is known about the effect of the axial ligand on other MN₄ compounds. When 16(Cl)FePc is coordinated to pyridine, the electron cloud is shared between the ligand and the Cl groups, which causes a change in the geometry of the catalyst and lowers its performance.

Materials and methods

Iron(II) phthalocyanine (FePc) and iron(II) 1,2,3,4,8,9,10,11,15,16,17,18,22,23,24,25-hexadeca(chloro) phthalocyanine (16(Cl)FePc) were supplied by Porphy Chem (Dijon, France). 4-Aminopyridine (Py), N,N-dimethylformamide (DMF), isopropyl alcohol, NaOH, and H₂SO₄ were obtained from Sigma (St. Louis, USA). Double-walled CNTs were provided by Nanocyl (Sambreville, Belgium). We chose working with double-walled CNTs instead of multi- or single-walled CNTs because of their higher purity (>90%).^{35,36} Similar to that in ref. 22, the functionalization of the CNTs with Py was obtained using the diazonium reaction. Briefly, 5 g of NaNO₂ was dissolved in 10 ml of H₂O; 7 g of Py was dissolved in 5 ml of 4 M HCl; and 0.1 g of CNTs was dispersed in 200 ml of DMF. The CNT dispersion was added to the NaNO₂ and Py solution. CNT-Py was collected by filtering. Next, CNT-Py was modified with either FePc or 16(Cl)FePc by refluxing in N₂ to obtain either CNT-Py-FePc or CNT-Py-(16)ClFePc. The ink formulation was obtained by dispersing 10 mg of CNT-Py-FePC or CNT-Py-(16) ClFePc in 1 ml of a mixture of 25% volume isopropyl alcohol and 75% H_2O . 10 µl of catalyst ink was loaded onto the surface of the electrode and let to dry (final loading was 0.1 mg cm^{-2}). The working electrode was a glassy carbon rotating ring disk electrode (GCE) of 4 mm diameter with a Pt ring from ALS (Tokyo, Japan). Electrochemical experiments were carried out on a Chi Instruments (Austin, USA) electrochemical bi-potentiostat. In RRDE experiments, the ring potential was set to 0.6 V vs. SCE. XPS data were recorded under a vacuum better than 5 imes10⁻¹⁰ mbar using a PHOIBOS-150 electron analyser (SPECS), Al Kα radiation and a constant pass energy of 20 eV.

Results and discussion

 MN_4 compounds are known for being stable in basic pH, but only a few authors have reported on the catalytic activity of MN_4 coordinated to a fifth ligand in an acidic environment.^{23,24,37,38} In Fig. 1a, we show the schematic structure and the electrochemical characterization in N₂ saturated 0.1 M H₂SO₄ solution of the CNTs modified with pyridine (CNT–Py) and of the FeN₄ used in this work (*i.e.* FePc and 16(Cl)FePc), in the absence and in the presence of the pyridine axial link. In all the voltammograms the redox peaks of the Fe(m)/(n) redox couple are highlighted. In the case of FePc, the Fe(m)/(n) redox peak appears at potentials close to 0.350 V νs . SCE. As mentioned above, the Fe(m)/(n) redox couple in 16(Cl)FePc has a higher redox potential compared to the unsubstituted FePc due to the presence of electron-withdrawing Cl atoms, which are distributed in all positions in the phthalocyanine ligand (0.610 V, Fig. 1a). The basicity of the carbon nanotube can also alter the electron density on the Fe centre by withdrawing electron density from the metal centre. The shift of Fe(m)/(n) transition to more positive values is favourable for ORR catalysis.^{4,30} Similar effects have been observed in graphitic carbon supports with different Lewis basicity, which also affects the electron density of the Fe centre. In addition, a linear relationship is found between the Lewis basicity of the graphitic support and the turnover frequency for the ORR on FeN_x/C sites, *i.e.*, the higher the basicity, the higher the turnover frequency.³⁹

In the presence of the pyridine moiety, the redox potential of the Fe(m)/(n) redox couple in FePc shifts around 40 mV towards more positive potentials as an effect of electron-pulling from the pyridine linker. Similar results were obtained for the CNT–Py-16(Cl)FePc catalyst (0.650 V, Fig. 1a). The mean values (obtained from five repeated experiments) of the redox potentials of the Fe(m)/(n) redox couples and surface concentration values of CNT–MN₄ and CNT–Py–MN₄ determined by the integration of the redox peak are summarized in Table 1.

XPS analyses confirm the existence of an oxidized state of Fe in CNT-Py-FePc (Fig. 1b). The spectrum that corresponds to FePc contains a sharp spin-orbit doublet (Fe $2p_{3/2} = 708.4$ eV and Fe $2p_{1/2} = 721.0$ eV) and broad features at 710.5 eV and 723.0 eV. Early investigations identified these broad features as shake-up satellites of the Fe²⁺ in the phthalocyanine.⁴⁰ Recent investigations have associated the sharp features with the presence of Fe²⁺ and the broad features appearing at higher binding energy as arising from the presence of a Fe³⁺ spin-orbit doublet.^{22,38} The corresponding binding energies of these broad features are fully compatible with those shown by the Fe 2p_{3/2} and Fe $2p_{1/2}$ core levels of Fe³⁺ species. The spectrum recorded from the CNT-Py-FePc sample does not show these sharp features but only a spin-orbit doublet characterized by binding energies (Fe $2p_{3/2} = 710.7$ eV and Fe $2p_{1/2} = 723.8$ eV) typical of Fe³⁺. The disappearance of the sharp features at lower binding energies in the Fe 2p spectrum of the CNT-Py-FePc sample and the shift of the spectrum to higher binding energies (as compared with the spectrum recorded from FePc) are compatible with a decrease in the electron density around the iron atom in the phthalocyanine structure. This suggests, as mentioned above, that in the pyridine sample there is a permanent displacement of the electron population of the iron atom due to the presence of this ligand. The Fe 2p XPS spectrum recorded from (16)ClFePc presents intense Fe³⁺ components and clear shoulders at 708.4 eV and 721.0 eV, indicating that this sample also contains a Fe²⁺ contribution. This component is, in any case, much smaller than the Fe²⁺ contribution observed in FePc. This implies that the electron density around the iron is lower in this sample compared to FePc, probably because it is displaced towards the Cl atom, which is in agreement with the voltammetric results shown in Fig. 1a. The spectrum corresponding to CNT-Py-(16)ClFePc shows a clear increase of the sharp Fe²⁺ features in comparison



Fig. 1 (a) Electrochemical characterization by cyclic voltammetry and schematic representation of CNT–FePc; CNT–Py–FePc; CNT–16(Cl) FePc; CNT–Py–16(Cl)FePc; and CNT–Py. Conditions: N₂ or O₂ saturated 0.1 M H₂SO₄ solution and a scan rate of 0.1 V s⁻¹ (b) XPS Fe 2p spectra of FePc; CNT–Py–FePc; 16(Cl)FePc; and CNT–Py–16(Cl)FePc.

with the spectrum of (16)ClFePc. This indicates that the addition of CNT–Py increases the electron density around the iron atom, contrarily to the observed in the CNT–Py–FePc sample. Nevertheless, the intensity of the Fe²⁺ contribution to the spectrum of CNT–Py–(16)ClFePc is lower than that to the spectrum of FePc, which implies that the CNT–Py–(16)ClFePc sample is an intermediate situation between FePc and CNT–Py– FePc.

ORR polarization curves are presented in Fig. 2a. In the presence of the axial ligand, the overpotential for the ORR is reduced by 80 mV. The onset potential of the electrocatalytic waves starts at 0.55 V for electrodes modified with CNT-Py-FePc and at 0.56 V for the CNT-Py-16(Cl)FePc. The coordination of both axial positions in FePc (octahedral complex geometry) is energetically much more favourable than single axial site coordination (square pyramidal geometry of the complex).²⁴

The total number of electrons determined by Koutecky– Levich extrapolation (inset, Fig. 2a) for the catalysts is summarized in Table 1. The pentacoordination favoured the $4e^-$ reduction process, as opposed to CNT–FeN₄, which promoted $2e^-$. The production of hydrogen peroxide was also corroborated by RRDE, as shown in Fig. 2b. In the absence of the axial ligand, more peroxide is formed. The CNT–16(Cl)FePc catalyst is the most active in terms of peroxide formation, while in the presence of the pyridine ligand very low amounts of peroxide are detected. The peroxide formed on electrodes only modified with CNT–Py is presented as a comparative reference.

Tafel plots exhibit slopes that vary from -0.085 V to -0.104 V dec⁻¹, which could be attributed to a mixture of two parallel mechanisms with different rate-determining steps. A schematic mechanism based on previous studies^{4,24,39,41} is presented in Scheme 1. The mechanism provides two pathways for the rate-determining step. The pathways are polarization dependent and consider that Fe²⁺ species are thermodynamically favour-able at high polarization. It must be noted that the reactions proposed in Scheme 1 are only possible mechanistic steps that occur after the rate-determining step.

As observed for FeN₄ macrocyclics adsorbed directly on graphite electrodes,^{15,27-29} for CNT–MN₄ and CNT–Py–MN₄, the onset potential for the ORR also appears close to the Fe(m)/(n) formal redox potential, so the reaction essentially starts when Fe(n) active sites are generated on the surface from the reduction of Fe(m). Fig. 2c shows the relationship between the formal potential of the catalysts and the catalytic activity expressed as log *I* (*E* = cte) normalized by FeN₄ surface concentration (*T*).

Table 1Fe(III)/(II) formal potential, Tafel slope, number of electrons transferred during the ORR, and surface concentration values determined bythe integration of the redox peaks of the Fe(III)/(II) redox couples for CNT-FePc; CNT-Py-FePc; CNT-16(Cl)FePc; or CNT-Py-16(Cl)FePc

Complex	$E_{(\text{Fe}(\text{III})/\text{Fe}(\text{III}))^{\circ}}$ (V vs. SCE)	Tafel slope (V dec^{-1})	No e ⁻	$\Gamma \text{ (mol cm}^{-2}\text{)}$
CNT-FePc	0.352 ± 0.004	-0.085 ± 0.012	2.56 ± 0.07	$1.62 imes 10^{-8}$
CNT-Py-FePc	0.395 ± 0.003	-0.098 ± 0.003	3.57 ± 0.02	$3.92 imes 10^{-9}$
CNT-16(Cl)FePc	0.613 ± 0.003	-0.104 ± 0.016	1.73 ± 0.02	$3.68 imes 10^{-8}$
CNT-Py-16(Cl)FePc	0.648 ± 0.006	-0.086 ± 0.002	3.45 ± 0.07	8.87×10^{-9}



Fig. 2 (a) Polarization curves recorded at electrodes modified with CNT–FePc; or CNT–Py–FePc; or CNT–16(Cl)FePc; or CNT–Py–16(Cl)FePc. Conditions: O_2 saturated 0.1 M H₂SO₄ solution, 400, 800, 1200, and 2400 rpm, and a scan rate of 0.005 V s⁻¹. (b) H₂O₂ oxidation measured at a Pt ring electrode when the disk was modified with CNT–16(Cl)FePc; or CNT–FePc; CNT–Py–FePc; CNT–Py–16(Cl)FePc; or CNT–Py. Conditions: O_2 saturated 0.1 M H₂SO₄ solution. A Pt ring polarized at 0.6 V, while the disk was rotating at 1200 rpm and a scan rate of 0.005 V s⁻¹. (c) Plots of catalytic activity as log *i*/*T* measured at 0.2 V vs. the formal potential of Fe(III)/(II) for CNT–FePc; CNT–Py–FePc; CNT–16(Cl)FePc; or CNT–Py–16(Cl)FePc; or CNT–Py–16(Cl)FePc. Conditions: O_2 saturated 0.1 M H₂SO₄ solution and 1200 rpm.



This confirms once more that regardless of the spatial configuration of the FeN₄ complexes, shifts of Fe(III/II) to more positive potentials are beneficial to the catalysis of the ORR, as the redox potential is a reactivity descriptor that predicts the increase of reactivity^{4,13,14,28,30} in these catalysts. Although this trend is

followed in the presence of the axial ligand that anchors the MN₄ complex to the CNTs, the increase in activity is more pronounced for FePc than for 16(Cl)FePc. Thus, the electron withdrawing groups reduce the gap between the energy of the frontier orbitals of the metal complex and the O2 molecule.4,43,44 The back-bonding processes could explain the difference between the behaviour of FePc and 16(Cl)FePc. When O₂ binds to the metal in MN₄, its 2p electrons interact with the partially filled d orbitals of the same. These processes are accompanied by intermolecular electron transfer, in which O₂ accepts charge density from the partially filled d orbitals of the metal via backbonding to the π^* antibonding orbital, and donates charge from a filled π molecular orbital to a half-filled dz orbital of the metal.^{2,11,12} The formation of the bond between O2 and Fe requires that the energies of the predominant d orbitals be the same as or similar to those of the charge transfer intermediate species.4,15,30,43 Therefore, the active site in the anchored complex is harder compared to the adsorbed catalyst. A hard active site in FePc and 16(Cl)FePc (from hard-soft acid base (HSAB) principle) would promote high activity for the ORR, as O₂ is a hard base.^{4,30,42,43} In the case of the CNT-Py-16(Cl)FePc derivative, the metal centre suffers the inductive effects of chlorine atoms located on the ligand, and the influence of the pyridine axial ligand, which promotes a higher oxidation state.¹⁰ However, this decrease in the electron density of the metal

centre, due to the chlorine atoms of the macrocyclic ligand and pyridine axial ligand, causes changes in the back-bonding processes, as well as the mismatch of the respective donoracceptor orbital energies, namely, less electronic coupling between the donor and the acceptor and less activity for CNT– Py–16(Cl)FePc systems compared to CNT–Py–FePc.

Conclusions

Likewise in nature, the fifth axial ligand plays a critical role in the increase of the catalytic activity of FePc and 16(Cl)FePc for the ORR in the trend CNT-MN₄ < CNT-Py-MN₄. The activity of FeN₄ can be tuned by changing the electron-withdrawing power of the ligand substituents on the macrocyclic ligand, which makes it possible to tune the donor-acceptor electronic coupling (Fe–O₂ adduct).^{1,24} The higher the separation between the energy of the frontier orbitals of the donor (FePc) and the acceptor (O₂), the lower the reactivity.⁴³ Thus, the electronwithdrawing groups reduce the gap between the energies of the frontier orbitals. However, when comparing CNT-Py-FePc with CNT-Py-16(Cl)FePc, the activity for CNT-Py-16(Cl)FePc was lower than the activity of CNT-Py-FePc. The lower increase in activity for CNT-Py-16(Cl)FePc in the presence of the back ligand compared to FePc is attributed to two pulling effects, namely the presence of the electron-withdrawing -Cl groups on the phthalocyanine ligand and the axial ligand, which operate simultaneously on the metal centre. This causes changes in the backbonding processes and the mismatching of the respective donor-acceptor orbital energies.

Finally, the presence of the conjugated axial ligand allows for the decoupling of the metal centre from the electrode surface, thereby changing the geometrical and electronic structure, which hinders the production of H_2O_2 and therefore explains the higher stability in acidic environments.

Acknowledgements

F. T. acknowledges the financial support of Fondecyt 11130167, and Dicyt 021342TG_DAS, and "Proyectos Basales". J. H. Z acknowledges the financial support of Millenium RC120001, Fondecyt 1140199 and Project Anillo CT-1412. F. J. R acknowledges the financial support of Fondecyt 1161117. I. P. acknowledges the financial support of PAI-CONICYT 79150041.

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