Biomimetic reduction of $O_2$ 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 phthalocyanine (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 $H_2O_2$. 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 $O_2$ and Fe, mismatching the energy of the frontier orbitals and lowering the activity towards the reduction of $O_2$.

Introduction

The oxygen reduction reaction (ORR) is an important process in fuel cells, but its sluggish kinetics gives rise to a high over-potential 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 (MN$_4$) belong to this class of catalysts. The role of MN$_4$ as a catalyst in the ORR$^{1-4}$ and other reactions$^{5-8}$ 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.$^{9-12}$ 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 MN$_4$ complexes with different carbon supports;$^{16-19}$ and (iii) the support of MN$_4$ complexes on different carbon nanostructures with or without coordination of a fifth ligand.$^{20-26}$ Already in the 70’s, Randin$^{13}$ and Beck$^{14}$ had proposed that the activity of MN$_4$ catalysts could be related to the M(III)/(II) 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 MN$_4$. On the other hand, electrocatalysts with increased activity and stability$^{21-24}$ 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 $O_2$ in acid, in the absence and in the presence of a pyridine axial ligand attached to the external walls of the CNTs. FeN$_4$ moieties were either absorbed directly onto the CNT by $\pi$ interactions (CNT–FeN$_4$) or coordinated to pyridine axial ligands previously attached to the CNT by diazonium salt modification (CNT–Py–FeN$_4$). Among the MN$_4$ catalysts, Fe-based MN$_4$ 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...
of H$_2$O$_2$ 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 MN$_4$ compounds. When 16(Cl)FePc is coordinated to pyridine, the electron cloud is shared between the ligand and the C1 groups, which causes a change in the geometry of the catalyst and lowers its performance.

**Materials and methods**

Iron(n) phthalocyanine (FePc) and iron(n) 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 H$_2$SO$_4$ 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 ($>90$%).$^{25,36}$ Similar to that in ref. 22, the functionalization of the CNTs with Py was obtained by the diazonium reaction. Briefly, 5 g of NaNO$_2$ was dissolved in 10 ml of H$_2$O; 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 NaNO$_2$ and Py solution. CNT–Py was collected by filtering. Next, CNT–Py was modified with either FePc or 16(Cl)FePc by refluxing in N$_2$ 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$_2$O. 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 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 x 10$^{-10}$ mbar using a PHOIBOS-150 electron analyser (SPECS), Al K$_z$ 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.$^{25,34,37,38}$ In Fig. 1a, we show the schematic structure and the electrochemical characterization in N$_2$ saturated 0.1 M H$_2$SO$_4$ solution of the CNTs modified with pyridine (CNT–Py) and of the FeN$_4$ 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 voltammmograms 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 vs. 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.$^{25,38}$ 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$_2$/C sites, i.e., the higher the basicity, the higher the turnover frequency.$^{29}$

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–MN$_4$ and CNT–Py–MN$_4$ 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 Fe$^{2+}$ in the phthalocyanine.$^{40}$ Recent investigations have associated the sharp features with the presence of Fe$^{2+}$ and the broad features appearing at higher binding energy as arising from the presence of Fe$^{3+}$ spin–orbit doublet.$^{25,38}$ 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 Fe$^{3+}$ 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 Fe$^{3+}$. 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 Fe$^{3+}$ components and clear shoulders at 708.4 eV and 721.0 eV, indicating that this sample also contains a Fe$^{2+}$ contribution. This component is, in any case, much smaller than the Fe$^{2+}$ 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 Fe$^{3+}$ features in comparison...
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 Fe$^{2+}$ 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).

The total number of electrons determined by R
to ech 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: N$_2$ or O$_2$ saturated 0.1 M H$_2$SO$_4$ 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.

![Fig. 1](image)

**Table 1**

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{Fe(II)/Fe(III)}$ (V vs. SCE)</th>
<th>Tafel slope (V dec$^{-1}$)</th>
<th>No $e^-$</th>
<th>$\Gamma$ (mol cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT–FePc</td>
<td>0.352 ± 0.004</td>
<td>−0.085 ± 0.012</td>
<td>2.56 ± 0.07</td>
<td>1.62 × 10$^{-8}$</td>
</tr>
<tr>
<td>CNT–Py–FePc</td>
<td>0.395 ± 0.003</td>
<td>−0.098 ± 0.003</td>
<td>3.57 ± 0.02</td>
<td>3.92 × 10$^{-9}$</td>
</tr>
<tr>
<td>CNT–16(Cl)FePc</td>
<td>0.613 ± 0.003</td>
<td>−0.104 ± 0.016</td>
<td>1.73 ± 0.02</td>
<td>3.68 × 10$^{-8}$</td>
</tr>
<tr>
<td>CNT–Py–16(Cl)FePc</td>
<td>0.648 ± 0.006</td>
<td>−0.086 ± 0.002</td>
<td>3.45 ± 0.07</td>
<td>8.87 × 10$^{-9}$</td>
</tr>
</tbody>
</table>
This confirms once more that regardless of the spatial configuration of the FeN₄ complexes, shifts of Fe(m/n) 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 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.

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 back-bonding to the π* antibonding orbital, and donates charge from a filled π molecular orbital to a half-filled dz orbital of the metal. 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.

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: O₂ 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; or CNT–Py–16(Cl)FePc; or CNT–Py. Conditions: O₂ 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/I measured at 0.2 V vs. the formal potential of Fe(m)/n for CNT–FePc; CNT–Py–FePc; CNT–16(Cl)FePc; or CNT–Py–16(Cl)FePc. Conditions: O₂ saturated 0.1 M H₂SO₄ solution and 1200 rpm.
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 donor–acceptor 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).13,14 The higher the separation between the energy of the frontier orbitals of the donor (FePc) and the acceptor (O2), the lower the reactivity.41 Thus, the electron-withdrawing 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 H2O2 and therefore explains the higher stability in acidic environments.

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Notes and references

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