

# Effect of Heat Treatment on the Redox Properties of Iron Porphyrins Adsorbed on High Area Carbon in Acid Electrolytes: An in Situ Fe K-Edge X-ray Absorption Near-Edge Structure Study

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Electronic aspects of an iron porphyrin, 5,10,15,20-tetrakis(4-methoxyphenyl)-21*H*,23*H*-porphine iron(III) chloride (FeTMPPCl) molecularly dispersed on a high area carbon black (Black Pearls 2000, BP) and then heat-treated (or thermally activated) at 800 °C in a flowing inert atmosphere, were investigated in situ in 1.0 M H<sub>3</sub>PO<sub>4</sub> by Fe K-edge X-ray near-edge structure (XANES). Profound differences were observed between the ex situ (dry) XANES of electrodes incorporating FeTMPPCl/BP before and after heat treatment and, likewise, in the case of the thermally treated FeTMPPCl/BP before and after immersion of the electrodes in the electrolyte. Monotonic shifts in the absorption edge toward higher energies were observed for heat-treated FeTMPPCl/BP as the potential was increased over a range of over 1 V. The overall magnitude of the shift, ca. 2.5 eV, was virtually the same as that obtained with non-heat-treated (or intact) FeTMPPCl/BP, which occurred in a much narrower potential range, ca. 0.2 V. In contrast to the behavior observed for the intact adsorbed macrocycle, its heat-treated counterpart displayed no affinity for CO, indicating that, to the level of sensitivity of this technique, iron sites in the thermally activated material are quite different from those in the N<sub>4</sub> environment of the intact macrocycle.

## Introduction

Transition-metal macrocycles, adsorbed on, or dispersed as, small microcrystallites, in high area carbon, and subsequently heat-treated at rather elevated temperatures (>600 °C) in an inert atmosphere, have been shown to enhance the rates of O<sub>2</sub> reduction in aqueous electrolytes.<sup>1–12</sup> In the case of supported macrocycles which exhibit catalytic activity for O<sub>2</sub> reduction without such treatment, the thermal activation has also been found to improve quite substantially the overall stability of operating O<sub>2</sub>-fed cathodes in alkaline solutions.<sup>13</sup> These phenomena have attracted much attention because of the following:

(i) Pt and Pt-based alloys, commonly used as O<sub>2</sub> reduction electrocatalysts in fuel cells applications, could be replaced by materials based on more abundant and less expensive elements.

(ii) The lack of affinity of these heat-treated materials toward carbon monoxide, as well as methanol, could help minimize problems associated with crossover of methanol (or CO generated by methanol reforming) to oxygen cathodes in solid polymer electrolyte fuel cells using Pt-based catalysts. As is well-known, CO adsorbs on Pt sites active for O<sub>2</sub> reduction, leading to losses in electrode performance.<sup>14</sup>

Despite extensive studies,<sup>1–12</sup> the evidence obtained by different research groups has led to conflicting views regarding the nature of the carbon-catalyst modifications responsible for the much improved electrochemical performance and/or stability of these heat-treated materials.

This paper presents ex situ and in situ Fe K-edge X-ray absorption near-edge structure (XANES) data which indicate

that the electronic and structural properties of FeTMPPCl adsorbed on Black Pearls high area carbon and later heat-treated at 800 °C in a flowing Ar atmosphere are substantially modified by simple exposure to a 1 M H<sub>3</sub>PO<sub>4</sub> solution. Furthermore, the position of the main absorption edge was found to increase linearly with the applied potential, ca. 2.5 eV/V, over a region spanning more than 1 V, pointing to the presence of redox active species in a multiplicity of chemical environments.

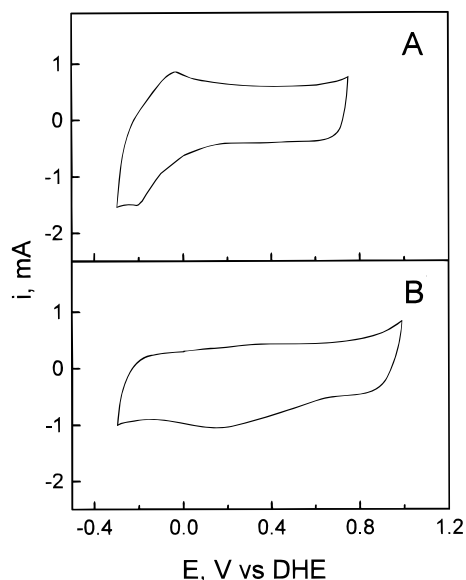
## Experimental Section

Black Pearls 2000 high area carbon (0.5 g, Cabot Corp., specific area 1500 m<sup>2</sup>/g), heat-treated at 800 °C in a furnace under flowing Ar (UHP, Matheson) at 1 atm pressure for 2 h, was allowed to equilibrate with a solution containing 50 mg of 5,10,15,20-tetrakis(4-methoxyphenyl)-21*H*,23*H*-porphine iron(III) chloride (FeTMPPCl, Aldrich Chemical) in 500 mL of acetone while stirring for 20 h. The mixture was then rapidly filtered using Whatman No. 2 filter paper and then dried at 110 °C in air. The amount of FeTMPPCl in the final mixture, determined gravimetrically, was ca. 22% w/w, which corresponds to about one-fourth of a monolayer of FeTMPPCl adsorbed on the carbon substrate, assuming a molecular area for FeTMPPCl of ca. 4 nm<sup>2</sup>. A fraction of this FeTMPPCl/BP mixture was firmly packed in a ceramic boat and covered with a nickel foil to minimize losses due to sublimation during the initial stages of the heat treatment. Otherwise, the thermal activation was performed under precisely the same conditions as those used for the pure carbon (see above) and removed from the furnace after the temperature had reached ca. 30 °C.

Electrodes were prepared by mixing about 2 mg of heat-treated FeTMPPCl/BP (and also, for comparison, non-heat-treated, or intact, FeTMPPCl/BP) with an emulsified Teflon

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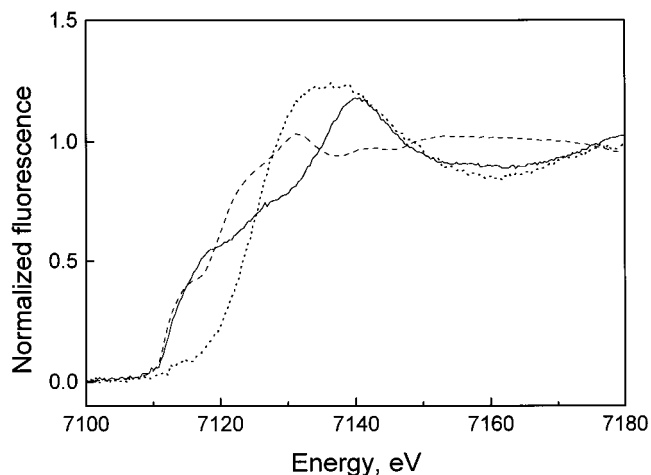
**Figure 1.** Cyclic voltammograms of Teflon-bonded electrodes (2 mg active material, 0.15 cm<sup>2</sup> projected area) containing intact (panel A) and heat-treated FeTMPPCl/BP (Panel B) in 1 M H<sub>3</sub>PO<sub>4</sub> recorded at a scan rate of 2 mV/s.

suspension (0.5 mg of PTFE solids, T30B, Dupont). The resulting paste was then pressed onto the end of a current collector (4 × 8 mm<sup>2</sup>, hydrophobic carbon layer, Eltech System). A dynamic hydrogen electrode in the same solution (DHE) incorporating two platinized Pt wires and placed in a compartment separated by sintered glass was used as a reference electrode. A detailed description of the cell may be found elsewhere.<sup>15</sup>

Experiments were conducted at room temperature in 1.0 M phosphoric acid prepared by diluting as-received 85% orthophosphoric acid (4 N, Aldrich Chemical) in Nanopure 18 MΩ water (Barnstead). XANES data were acquired at Beamline 4-1 at the Stanford Synchrotron Radiation Laboratory (SSRL) operating at an energy of 3 GeV with a ring current of 60–100 mA. The beam was monochromatized with a set of two Si(111) crystals with the exit slit adjusted to 1 × 6 mm<sup>2</sup>. All of the measurements were performed in the fluorescence mode using a Lytle-type ionization detector purged with Ar with a three-absorption-length Mn filter. The energy was calibrated using the first inflection point (7112 eV) of an iron foil of one absorption length recorded in the transmission mode and denoted hereafter as  $E_{\text{Fe}}$ . The position of the Fe absorption edge of the specimens examined in this work is expressed in terms of  $\Delta E_{\text{edge}} = E_{\text{edge}} - E_{\text{Fe}}$ , where  $E_{\text{edge}}$  is defined as the energy at which the normalized absorption is precisely one-half. Virtually identical experiments were performed at NSLS (X23-A2) at  $E_{\text{ring}} = 2.56$  GeV,  $160 < i_{\text{ring}} < 350$  mA, with the beam monochromatized with Si(311) crystals. The fluorescence radiation in that case was measured with a PIN diode with an Al filter in the current mode. Experiments involving carbon monoxide binding were performed by bubbling CO (UHP, Matheson) through the phosphoric acid solution for more than 2 h.

## Results and Discussion

**Electrochemistry.** The cyclic voltammograms of Teflon-bonded electrodes containing intact and thermally activated FeTMPPCl/BP in 1 M H<sub>3</sub>PO<sub>4</sub>, recorded at a scan rate of 2 mV/s are shown in panels A and B of Figure 1. As has been reported in earlier publications,<sup>16,17</sup> the intact adsorbed macrocycle displays a set of well-defined redox peaks with an average



**Figure 2.** Fe K-edge X-ray absorption near-edge structure (XANES) of heat-treated FeTMPPCl/BP as a dry powder (ex situ, solid line) and incorporated into the Teflon-bonded electrode in contact with 0.1 M H<sub>3</sub>PO<sub>4</sub> under no potential control (ca. 0.6 V vs DHE, in situ, dotted lines). Also shown in this figure is the ex situ XANES of an Fe foil for comparison (dashed line).

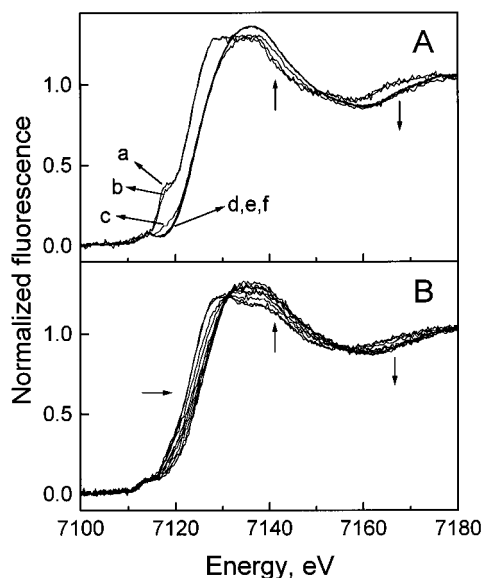
potential  $E_0 = -0.1$  V vs DHE. In contrast, the thermally activated counterpart shows a very ill-defined broad feature centered at about 0.2 V (maxima at ca. +0.3 V in the anodic scan and at ca. +0.1 V in the cathodic scan) superimposed on the large capacitive background, with no other noticeable features. The imbalance in charge comparing the scans in the positive and negative directions is due to the reduction of adventitious residual oxygen and, at the more negative potentials, to hydrogen evolution, especially for intact FeTMPPCl/BP (see panel A). On the basis of these results, it may be concluded that the thermal activation substantially modifies the electronic properties of the original adsorbed macrocycle.

### In Situ X-ray Absorption Near-Edge Structure (XANES).

Figure 2 compares the Fe K-edge XANES of heat-treated FeTMPPCl/BP as a dry powder (ex situ, solid line) and incorporated into the Teflon-bonded electrode in contact with 1.0 M H<sub>3</sub>PO<sub>4</sub> under no potential control (in situ, dotted line). On the basis of the striking differences observed for the dry powder and the electrode in situ, it becomes evident that *no conclusions regarding the nature of the electrocatalytic site can be drawn based purely on ex situ data of the dry material.*

Also noted during these measurements was a reduction in the magnitude of the (unnormalized) edge jump, ca. 6%, after the electrode containing the heat-treated FeTMPPCl had been exposed for 90 min to 1.0 M H<sub>3</sub>PO<sub>4</sub>. The most likely explanation for this effect is the dissolution of at least part of the iron in the material into the bulk electrolyte away from the X-ray beam.

The near coincidence of the onset of the edge at 7110 eV between the dry material and that of an Fe foil (see dashed line in this figure) suggests that the dry heat-treated FeTMPPCl/BP contains iron in elemental form. This may not be surprising as carbon can act as a reducing agent at these high temperatures. Similar observations have been reported recently by Martins Alves et al.<sup>11</sup> for cobalt phthalocyanine and by Faubert et al. for Fe and Co porphyrins by X-ray photoelectron spectroscopy and X-ray diffraction.<sup>12</sup> Since the XANES is governed both by electronic and structural effects, it seems conceivable that the differences in the spectral properties of thermally activated FeTMPPCl/BP in this spectral region and those of the Fe foil may be due to differences in the particle size.<sup>18</sup> Another species



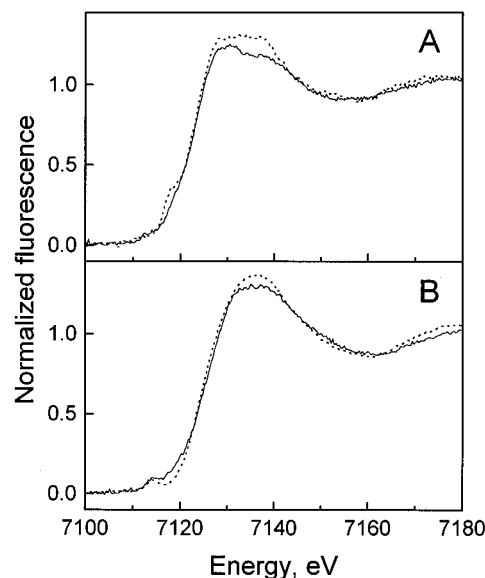
**Figure 3.** Series of in situ Fe K-edge XANES for intact (panel A) (a)  $-0.35$ , (b)  $-0.20$ , (c)  $0.00$ , (d)  $0.30$ , (e)  $0.60$ , and (f)  $0.90$  V vs DHE and heat-treated FeTMPPCl/BP as a function of potential in  $0.1$  M  $\text{H}_3\text{PO}_4$  (panel B). The arrows point in a direction of increasing potential for data collected at  $-0.20$ ,  $0.00$ ,  $0.20$ ,  $0.30$ ,  $0.50$ ,  $0.60$ ,  $0.80$ ,  $0.90$ , and  $1.15$  V vs DHE.

that may be formed by the thermal activation is iron carbide for which the XANES spectrum is similar to that of metallic iron.<sup>19</sup>

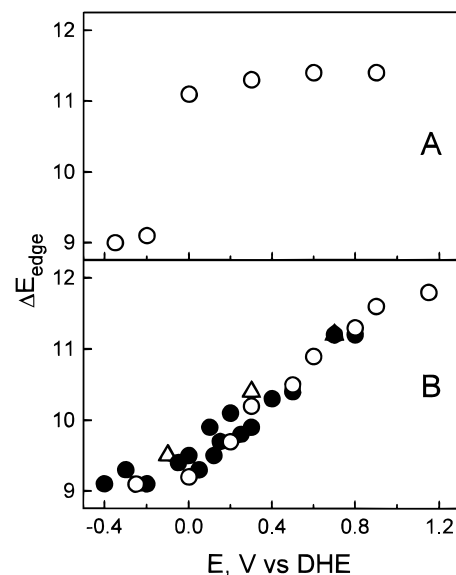
Upon contact with water during the preparation of the electrode and/or with the  $1.0$  M  $\text{H}_3\text{PO}_4$  solution during the experiments, a large fraction of the elemental Fe oxidizes to yield yet-to-be-identified species on the surface and/or dispersed in the carbon matrix. These may include nitrogen-coordinated Fe centers, iron oxides, and various forms of iron phosphates, which by themselves or in concert would be responsible for the high electrocatalytic activity of the heat-treated materials for dioxygen reduction.

Insight into the electrochemical properties of thermally activated FeTMPPCl/BP was gained by performing a series of in situ XANES measurements as a function of potential (see panel B, Figure 3, and caption for details). The corresponding data for the intact material are shown in panel A in the same figure. The large differences that exist between the in situ XANES of intact (dotted lines) and heat-treated FeTMPPCl/BP (solid lines) are better illustrated in panels A and B of Figure 4, for electrodes polarized at  $-0.2$  and  $0.9$  V, respectively.

Plots of  $\Delta E_{\text{edge}}$  vs potential extracted from data of the type shown in Figure 3 are given in Figure 5 for the non-heat-treated (panel A) and heat-treated FeTMPPCl/BP (panel B), over the ranges  $-0.35 < E < 0.90$  and  $-0.40 < E < 1.20$  V vs DHE, where the solid and open circles (SSRL) and triangles (NSLS) in panel B are based on results for the heat-treated FeTMPPCl/BP in three completely independent runs. Within the uncertainty of these measurements, the dependence of  $\Delta E_{\text{edge}}$  on the applied potential in the range  $0.0 < E < 1.2$  V is fairly linear ( $2$  eV/V) and quite reproducible. This behavior is unlike that observed for the intact form of FeTMPPCl/BP, which displays a sharp transition, within ca.  $0.2$  V, between the two oxidation states (see panel A). However, the overall shift in  $\Delta E_{\text{edge}}$ , ca.  $2.5$  eV, is almost identical for both the intact and heat-treated species and corresponds to a net oxidation state change of a single electron per iron site. The rather broad potential range over which the shift occurs is most likely due to the presence of an



**Figure 4.** Comparison between the in situ Fe K-edge XANES of FeTMPPCl/BP before (dotted lines) and after heat treatment (solid line) at  $-0.2$  V (panel A) and  $0.9$  V vs DHE (panel B) from the data in Figure 3.



**Figure 5.** Plots of  $\Delta E_{\text{edge}}$  ( $= E_{\text{edge}} - E_{\text{Fe}}$ , where  $E_{\text{edge}}$  is defined as the energy at which the normalized absorption is precisely one-half, and  $E_{\text{Fe}} = 7112$  eV, is the first inflection point of the XANES of metallic iron), vs potential extracted from data of the type shown in Figure 3 for intact (panel A) and heat-treated FeTMPPCl/BP (panel B), over the ranges  $-0.35 < E < 0.90$  and  $-0.40 < E < 1.20$  V vs DHE. The open and solid circles and triangles represent data acquired at SSRL and NSLS, respectively, in three completely independent measurements.

ensemble of sites with similar electronic properties and, thus, redox potentials. This interpretation is consistent with the voltammetry, which showed an extremely broadened set of peaks.

Attempts were made to examine the affinity of the thermally treated FeTMPPCl/BP for carbon monoxide by purging CO into the solution while polarizing the electrode at  $-0.2$  V vs DHE for 2 h. In the results obtained (not shown in this work), no changes in the in situ Fe K-edge XANES could be detected. This behavior is in direct contrast to that observed for intact FeTMPPCl/BP, which displayed a shift in the absorption edge toward higher energies, as well as the emergence of two new peaks in the preedge region, which are attributed to the formation

of a  $L(\text{FeTMPPCl})\text{CO}$  adduct,<sup>20</sup> where L is water. On this basis, it seems highly unlikely that the  $\text{Me}-\text{N}_4$  environment of the original macrocycle remains intact after the thermal activation, as has been suggested in the literature.<sup>7</sup>

It is also interesting to note that the relatively positive potentials at which the  $\text{Fe(II)}$  of the heat-treated material begins to appear (ca. +0.8 V vs DHE) are consistent with the relatively positive potentials at which oxygen is reduced at significant current densities in  $\text{H}_3\text{PO}_4$ -equilibrated Nafion fuel cells at ca. 125 °C using very similar catalysts (e.g., ca. 0.8 V vs a reversible hydrogen electrode, in contact with the same membrane, at a current density of 100  $\text{mA}/\text{cm}^2$ ).<sup>21</sup> Even though the latter were carried out at elevated temperatures, it appears likely that  $\text{O}_2$  reduction is catalyzed by  $\text{Fe(II)}$  in a redox mediation-type mechanism, in a fashion similar to that proposed by Shigehara and Anson for intact Fe porphyrins supported on graphite.<sup>22</sup>

The observed shifts in the Fe absorption K-edge, which provides a direct measure of the oxidation state of the metal site, indicate that the onset for the reduction of the ferric sites in the heat-treated macrocycle occurs at about 0.9 V vs DHE and thus at much more positive potentials than that observed for the intact form of the macrocycle, ca. 0.0 V vs DHE. This information would thus be consistent with the much higher activity of the heat-treated materials for dioxygen reduction (lower overpotentials) compared to their intact counterparts.

## Summary and Conclusions

The results presented in this investigation provide for the first time in situ evidence that the thermal activation of a metal macrocycle adsorbed on a high area carbon in concentrated acid solutions produces an ensemble of sites with redox potentials spread over a wide potential range. This behavior is not only unlike that observed for the intact adsorbed macrocycle but suggests that the electronic and structural environment surrounding iron is markedly different from that found in intact porphyrins. This view was supported by the lack of affinity of thermally activated  $\text{FeTMPPCl/BP}$  for carbon monoxide when polarized at very negative potentials, for which the in situ XANES were virtually identical before and after bubbling CO into the solution. As shown in recent work in this laboratory, CO binds to the reduced form of intact adsorbed  $\text{FeTMPPCl}$  on BP to yield characteristic features in the preedge region. On this basis, it seems highly unlikely that  $\text{Me}-\text{N}_4$  groups of the type suggested in the literature,<sup>7</sup> if at all present, may play a significant role as the active site for  $\text{O}_2$  reduction.

Although the data reported in this work are insufficient to identify the precise nature of the sites responsible for the electrocatalytic activity of heat-treated  $\text{FeTMPPCl/BP}$  (and perhaps other related iron macrocycles as well), it becomes evident from a comparison between the XANES obtained before (ex situ) and after (in situ) exposure to the electrolyte that only in situ measurements can yield, at least for this kind of system, information of relevance to electrocatalysis. In addition, it appears that one of the beneficial properties imparted by the heat treatment is the creation of iron sites *upon contact with the electrolyte*, which can be reduced at potentials significantly

more positive than those observed for the intact macrocycle, yielding highly catalytic  $\text{Fe(II)}$  sites for  $\text{O}_2$  reduction.

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