

## Electrocatalytic Reduction of Nitrite by Iron Phthalocyanine Monolayer Irreversibly Adsorbed on the Edge Plane of Pyrolytic Graphite

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Received February 24, 1998

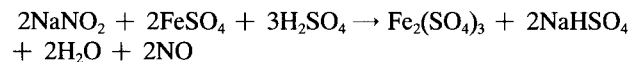
Nitrite is a species that promotes corrosion when dissolved in water,<sup>1</sup> a major component of waste after the waste decontamination in a nuclear power production,<sup>2</sup> and also involved in a bacterial process known as nitrogen cycle.<sup>3</sup> The detection of nitrite, therefore, is important from an environmental and biological point of view. Methods based on electrochemical principles offer some merits over other techniques in the sense that they provide an easy and convenient way of detection as well as high sensitivity. Since the overpotential of nitrite reduction at ordinary solid electrodes is very high, much effort has been directed to look for good electrocatalysts. Meyer *et al.*<sup>4</sup> have long studied the reduction mechanism by metallic complexes in a solution phase. They found EDTA complexes of Ru(II) and Fe(II) had a high catalytic activity toward nitrite reduction. They also found a small amount of Fe(III)-porphyrin dissolved in water exhibited a high activity.<sup>5,6</sup> Recently they reported thin polymeric film<sup>7</sup> made by polymerization of Fe(III)-protoporphyrin IX dimethyl ester in organic solvents could be used for the same purpose. On the other hand Anson *et al.*,<sup>8</sup> in their efforts to develop a robust catalyst, used Fe-substituted heteropolytungstates to reduce nitrite directly to ammonia. While most attempts so far have been focused on the use of thin film or homogeneous electrocatalysts, we have sought the possibility of using a *monolayer* of electrocatalysts adsorbed on solid electrodes. Phthalocyanine (Pc) complexes of transition metals could be good candidates because they provide a binding site through which nitrite can be activated. Moreover their electrochemical behavior<sup>9-11</sup> has been well studied by a number of people over a wide range of pH in an aqueous solution as well as organic media, especially in connection with oxygen reduction.<sup>12-14</sup> Undoubtedly, these facts are expected to provide unambiguous interpretation of results in the present study.

### Experimental Section

All the chemicals (Aldrich Chemical Co.) were of reagent grade or better and used without further purification. Nitrite solutions of various concentrations were prepared by dissolving sodium nitrite in 0.5 M sulfuric acid just before use. 18 Mohm deionized water (Millipore Co.) was used for preparing solutions and for washing. Adsorption of FePc onto the edge plane of OPG (ordinary pyrolytic graphite, Union Carbide) was effected by dipping the electrode for a given amount of time in a DMSO solution of  $10^{-4}$  M FePc, followed by immediate washing in macrocycle-free DMSO and then in water. Surface coverage was controlled by simply changing dipping time. This procedure was repeated at least three times before taking an average. In each ex-

periment, the electrode was ground against 1200 grit SiC paper to ensure the fresh surface and subject to sonication.

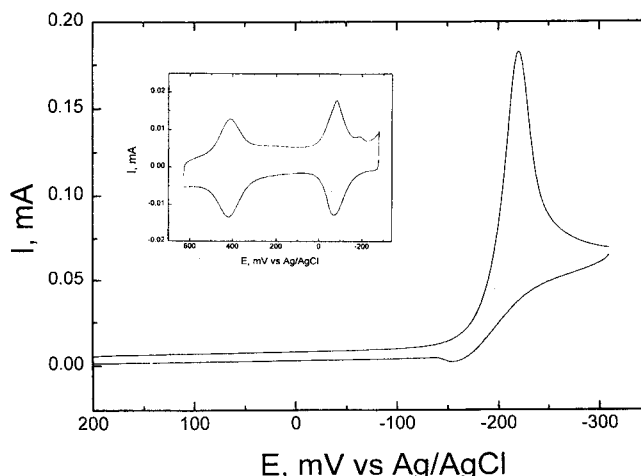
Fe(NO)Pc, the nitrosyl complex of FePc, was synthesized by a direct reaction of NO with FePc according to the literature.<sup>15</sup> Fe(NO)Pc formation was confirmed by a strong NO stretching peak at  $1685\text{ cm}^{-1}$ . NO was produced by mixing an equal amount of FeSO<sub>4</sub> and NaNO<sub>2</sub> solutions prepared in 1 M sulfuric acid according to the following reaction.<sup>16</sup>



A typical three electrode cell and data acquisition systems (BAS 100BW) were employed for the electrochemical measurements throughout the experiments. A Ag/AgCl electrode and a platinum coil were used as a reference and counter electrode, respectively. All the measurements were carried out at room temperature.

### Results and Discussion

Figure 1 shows cyclic voltammograms of FePc (inset) at a full coverage and the reduction of nitrite in 0.5 M sulfuric acid at a FePc covered electrode. Two peaks centered at +0.42V and -0.08V have been assigned, respectively, to redox processes involving the central metal ion, Fe(III)Pc(-2)/Fe(II)Pc(-2) and Fe(II)Pc(-2)/Fe(II)Pc(-3) although a possibility of the formation of Fe(I)Pc(-2) was presented in an

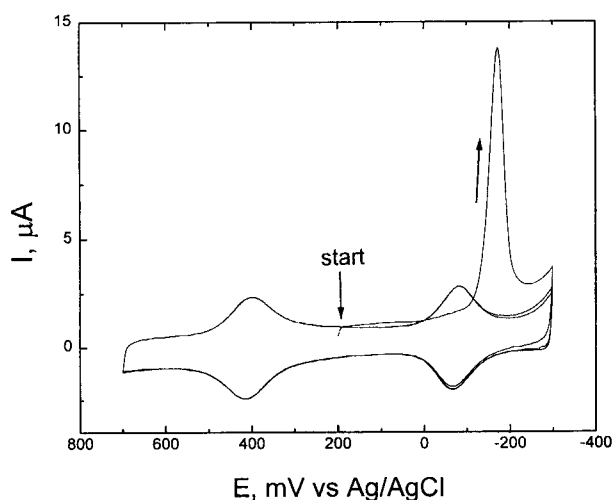


**Figure 1.** Cyclic voltammogram for the nitrite reduction by FePc ( $\Gamma=1.0 \times 10^{-9}\text{ mol}\cdot\text{cm}^{-2}$ ) adsorbed at the edge plane of pyrolytic graphite in Ar-saturated 0.5 M sulfuric acid.  $C_{\text{NO}_2^-}=5\text{ mM}$ ; Scan rate= $200\text{ mV}\cdot\text{s}^{-1}$ ; Apparent electrode area= $0.062\text{ cm}^2$ . Inset: Cyclic voltammogram for FePc under the same condition except that the solution does not contain nitrite; Scan rate= $100\text{ mV}\cdot\text{s}^{-1}$ .

acidic solution.<sup>10</sup> The coverage of FePc determined by integration of the peak(s) was about  $1.0 \times 10^{-9}$  mol  $\text{cm}^{-2}$ . When compared with the adsorption of tetrasulfonated FePc ( $3.0 \times 10^{-11}$  mol  $\cdot$   $\text{cm}^{-2}$ ) on the basal plane of HOPG (highly oriented pyrolytic graphite), this value was found to be much larger although the molecular size was taken into consideration. This is due to the fact that the effective surface area of the edge plane of OPG is larger than that of the basal plane of HOPG because of the higher surface roughness and thus accommodates a higher loading of macrocycles. Interfacial capacitance determined from cyclic voltammetry certainly reflects this fact. The value of  $290 \mu\text{F} \cdot \text{cm}^{-2}$  for the edge plane of OPG is much larger than that observed for HOPG(bp) (ca.  $3 \mu\text{F} \cdot \text{cm}^{-2}$ )<sup>17</sup> and even larger than those of reported values for the edge plane of HOPG ( $50\text{--}70 \mu\text{F} \cdot \text{cm}^{-2}$ ).<sup>18</sup> However, the adsorbed amount was not precisely proportional to the surface area, probably because of the large molecular size of FePc, compared to the surface roughness.

Nitrite reduction was found to proceed in acidic solutions and stopped when solutions were made alkaline. Since higher catalytic activity was found as the solution acidity increased, we confined our study in 0.5 M sulfuric acid. Among two redox couples, Fe(II)Pc(-2)/Fe(II)Pc(-3) is responsible for the nitrite reduction. This was confirmed by the following experiments: while no reduction of nitrite was observed when potential was cycled between 0.2 and 0.6 V, a negative scanning from 0.2 V beyond the reduction peak of Fe(II)Pc(-2) to Fe(II)Pc(-3) gave an irreversible reduction peak of nitrite. Since nitrite undergoes a rapid disproportionation reaction in strong acidic media to NO and nitrate and nitrate is not electrochemically reduced, nitrite reduction is believed to take place via the reduction of NO by forming Fe(II)(NO)Pc(-2) complex in which NO is bound as an axial ligand.

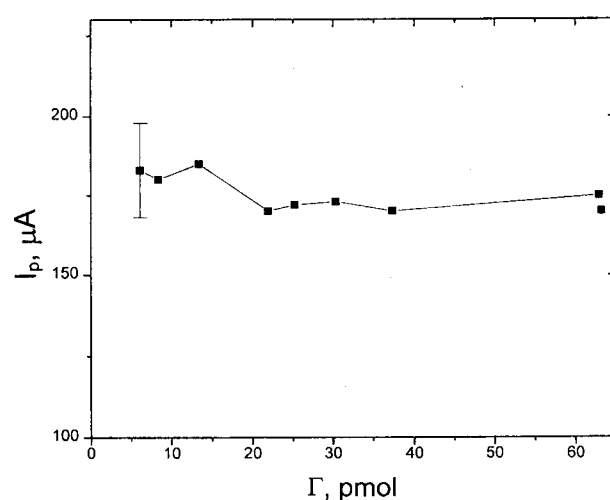
The formation of this complex was confirmed when compared with the voltammetry of the synthesized Fe(NO)Pc monolayer under the same conditions. Figure 2 shows that Fe(NO)Pc displayed a totally irreversible reduction peak during the first scan when potential was excursed beyond the



**Figure 2.** Cyclic voltammogram of Fe(NO)Pc adsorbed on the edge plane of pyrolytic graphite in 0.5 M sulfuric acid. Scan rate:  $50 \text{ mV} \cdot \text{s}^{-1}$ .

reduction potential of Fe(II)Pc(-2) at the same potential as that when nitrite was in the solution. This observation tells that NO reduction is associated with the formation of Fe(II)Pc(-3) species. The reason why reduction of NO took place only during the first scan is because the product(s) is removed from the surface to the bulk phase, leaving iron site unbound. Subsequent scans restored a characteristic behavior of FePc. This is somewhat distinct from the porphyrin case, where Fe(III)-NO complex<sup>7</sup> is first formed and charge transfer from NO to  $\text{Fe}^{3+}$  takes place, making ferrous state. The fact that the scan direction did not affect voltammetric behavior as long as the scan was initiated at more positive values than NO reduction potential indicates Fe(III)(NO)Pc(-2) is a stable adduct. Although the reaction product(s) is not known at this stage, in analogy with iron porphyrin cases the ammonium ion may be the major product, with other mononitrogen compounds as minor species.<sup>6,7</sup> Production of dinitrogen compounds such as hydrazine,  $\text{N}_2\text{O}$ , and  $\text{N}_2$ , however, may not be favorable because the residence time of mononitrogen compounds on the surface which leads to N-N coupling is short. Various dinitrogen species, however, have been detected in a thick layer such as an electropolymerized film containing iron(III) protoporphyrin IX dimethyl ester. A large reduction current shows FePc is a very efficient electrocatalyst although similar behavior was observed in the case of cobalt phthalocyanine.

Figure 3 is a plot of peak currents of nitrite reduction as a function of surface coverage. To our surprise, almost the constant peak currents within an experimental error were observed when the coverage was changed. A higher coverage does not necessarily mean higher catalytic activity. We envision this observation as kinetic vs diffusion control. If charge transfer rate from the electrode to Fe(NO)Pc is much faster than mass transport rate by diffusion by which NO is supplied to the electrode, the rate is determined by diffusion and thus overall current is controlled by it. Surface diffusion, in this case, does not affect overall rate constant since time required for NO moves from a point on the surface to FePc is probably very short, compared with diffusion time from the solution. Experiments where mass tran-



**Figure 3.** Plot of the coverage of FePc vs peak current for the nitrite reduction in 0.5 M sulfuric acid.  $C_{\text{NO}_2^-} = 5 \text{ mM}$ ; Scan rate =  $100 \text{ mV} \cdot \text{s}^{-1}$ .

sport rate is made very fast may reveal the detailed knowledge of this process. Measurements with a rotating disk electrode is in progress and will be reported in due course. We hope to distinguish contribution by kinetic or surface diffusion to overall current from mass transport rate. The arguments based on FePc multilayer formation and thus the decrease in the effective number of FePc exposed to the solution dose not hold in this case since FePc is not likely to form a multilayer and this phenomenon was also observed when the coverage was far below monolayer. Although nitrite reduction was independent of surface coverage of FePc, reduction current at a constant amount of catalyst showed a linear dependence on a tested range of nitrite concentration (0.08 to 20 mM) as expected. Our experiments may imply important aspects in the practical applications. A minimum amount of electrocatalyst is needed to get full catalytic activity as long as one can be sure that electron transfer rate overrides diffusion or any other mass transport processes.

In this work, we showed FePc is a very efficient catalyst for the nitrite reduction in acidic solutions and Fe(II)Pc(-2)/Fe(II)Pc(-3) pair is responsible for such a high activity. Also we showed the reduction current is independent of the surface coverage within our experimental conditions and explained this effect in terms of kinetic vs diffusion control.

**Acknowledgment.** The author thanks Dr. I. T. Bae at Case Western Reserve University for the discussion. Financial support from Korea Research Foundation (04D0071) is gratefully acknowledged.

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## A Study on the Relationships between Molecular Structure and Antitumor Activity II: *Ab Initio* Study on 1-(2-Chloroethyl)-3-cyclohexyl-1-nitrosourea (CCNU)

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Received February 25, 1998

The nitrosoureas form a class of compounds with tumor-inhibitory property and they derive their clinical usefulness from high lipophilicity together with low toxicity.<sup>1</sup> The chloroethylnitrosoureas which have been of clinical importance are 1,3-bis(2-chloroethyl)-1-nitrosourea (BCNU, carmustine), 1-(2-chloroethyl)-3-cyclohexyl-1-nitrosourea (CCNU, lomustine), 1-(2-chloroethyl)-3-(4-methylcyclohexyl)-1-nitrosourea (MeCCNU), 1-(2-chloroethyl)-3-(2,6-dioxo-3-piperidyl)-1-nitrosourea (PCNU).<sup>2,3</sup>

Especially, the CCNU displays therapeutic activity against brain tumors, colorectal tumors, Hodgkin's disease, multiple myeloma, gastrointestinal carcinoma, lung carcinoma, and prostate tumors.<sup>4-6</sup> The antitumor activity of nitrosoureas is closely related with their alkylation activity<sup>7,8</sup> and solubility.<sup>9</sup> Under physiological conditions, it was proposed that chloroethylnitrosoureas decompose to produce chloroethylcarbonium ions or diazonium hydroxides which function as the alkylating agents.<sup>2</sup> Because N-nitroso group in nitrosoureas