

Electrocatalytic Reduction of Sulfur Dioxide by Iron Phthalocyanine Monolayer in Acidic Conditions

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The iron phthalocyanine (FePc) monolayer adsorbed on a graphite surface showed a remarkable activity for the SO₂ reduction in aqueous conditions. The highest activity was observed at strongly acidic solutions and decreased with a pH increase due to the H⁺ limitation of reduction. Only SO₂ and HSO₃⁻ are reducible forms. The reduction mechanisms at strongly and moderately acidic conditions were suggested. The SO₂ reduction current was independent of the surface coverage and the ppb level detection was possible with amperometry.

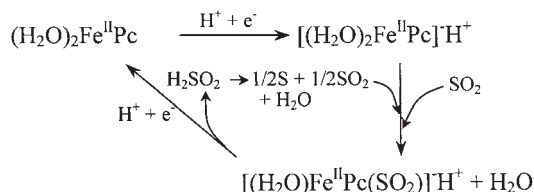
Electrochemical reactions of sulfur dioxide have attracted much attention for their wide range of applications¹⁻³ such as energy generation, dithionite production, and electrowinning of sulfide ores. While most studies have been directed toward the oxidation⁴⁻⁶ at various metal electrodes both in aqueous and nonaqueous solvents, the research on reduction is relatively rare. In aprotic solvents, SO₂ undergoes a reversible one-electron reduction. Sawyer et al.⁷ showed that the formed SO₂⁻ binds to SO₂ to make a blue-colored species or dimerizes to dithionite ion in a DMF solution. In aqueous media,⁸ however, SO₂ undergoes two-electron reduction, exhibiting a well-defined, diffusion-controlled voltammetric response under highly acidic conditions. The reduction product, H₂SO₂, is unstable and disproportionates to SO₂ and elemental sulfur whose presence was confirmed by the voltammetric peak of Hg^{II}S on a mercury electrode. In early polarographic studies, Kolthoff and Miller⁹ suggested the change in the reduction mechanism as pH increased. Most recent researches have been done using a Pt electrode. Quijada et al.¹⁰ showed that SO₂ was irreversibly adsorbed on both single- and poly-crystalline Pt surfaces in a sulfuric acid medium. The reduction proceeds in two steps at a polycrystalline Pt surface where the adsorbed SO₂ is reduced before the reduction of solution phase SO₂ takes place, yielding elemental sulfur and polysulfide as ultimate products.

While most researches to date have been carried out using pure metallic electrodes in which a rather large overpotential is required, we have tried to find efficient electrocatalysts made of metallomacrocycles. Among many candidates, FePc, which has been best known as an oxygen reduction catalyst and also found in our group to be an excellent electrocatalyst for NO reduction,¹¹ was applied to the SO₂ reduction in this work. We pursued the characteristic behavior of SO₂ reduction as a function of pH as well as the possibility of this system functioning as a direct electrochemical sensor in a ppb range.

SO₂ solutions were prepared either from SO₂ gas or from Na₂SO₃ just before use. Since the voltammetric features were exactly the same, we used Na₂SO₃ to precisely adjust sulfite (or equivalently SO₂) concentration. Adsorption of FePc was effected onto the edge plane of the ordinary pyrolytic graphite

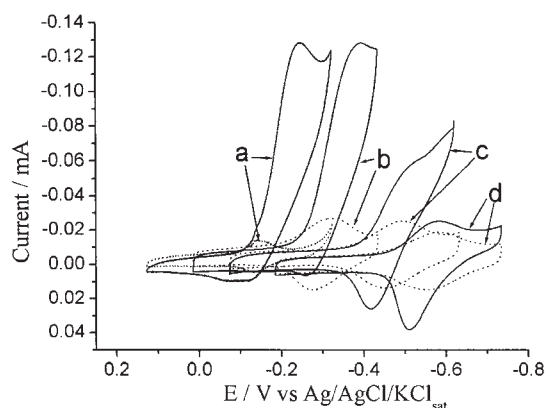
by dipping the electrode for a given period of time in a DMSO solution of FePc, followed by immediate washing in FePc-free DMSO and then in the electrolyte. The surface coverage was controlled by changing dipping time. In each experiment, the electrode was ground against 1200 grit SiC paper and subject to sonication to ensure the fresh surface. For an amperometric detection of SO₂, potential was applied where the reduction takes place and current was measured while rotating the electrode. The SO₂ concentration was varied by the stepwise addition of the concentrated solution into the SO₂-free solution. All the experiments were carried out in buffer solutions at room temperature.

Figure 1 shows a series of cyclic voltammograms of SO₂ (2 mM) reduction by the FePc-adsorbed electrode at different pHs. It is evident that [Fe(II)Pc(-3)]⁻, a reduced form of Fe(II)Pc(-2), exhibits electrocatalytic activities whose peak potential moves by 60 mV per pH. The reduction is energetically favorable by ca. 200 mV compared to the bare electrode. Contrast to the case in a nonaqueous solution, the reduction is highly irreversible. The reduction current remains constant roughly up to pH 3 and then decreases as the solution pH increases, indicating both SO₂ and HSO₃⁻ are irreversibly reduced in strongly acidic conditions. No reduction wave was observed above pH 7. The reduction is diffusionally controlled with elemental S as a final product. The following reduction scheme could be written with the formation of sulfoxylic acid, which disproportionates to SO₂ and S.



For a rapid decrease in current in moderately acidic conditions, Kolthoff and Miller argued that it was due to the pH effect on the position of equilibrium between two tautomeric forms of H₂SO₃. This explanation, however, may not be plausible as the equilibrium constant for the reaction, SO₂ + H₂O = H₂SO₃, is known to be infinitesimally small.¹² We attribute this to the limitation to H⁺, which is the requisite for the SO₂ reduction. To confirm this reasoning, we tried with more concentrated SO₂ solution (20 mM) and obtained the same current-pH pattern but with a current drop at an early stage. That is because more H⁺ is required to reduce higher concentration of SO₂.

In weakly acidic conditions beyond pH ca. 5, the oxidation current was observed. This oxidation peak increases with a pH increase although the reduction current rapidly drops down. We attribute this to the formation and oxidation of dithionite ion. Dithionite is very unstable in strongly acidic media but could be



formed in weakly acidic media from HSO_2^- , which is produced by the reduction of HSO_3^- . This explanation can be justified from the fact that the same voltammetric feature was obtained by dissolving $\text{Na}_2\text{S}_2\text{O}_4$ in the electrolyte. The following reduction scheme is written for $\text{pH} > 5$.

to that of SO_2 in solution to the electrode. In our case, it is not easy to exactly calculate the distance between FePc molecules at a submonolayer coverage due to the very rough nature of the surface, but at least up to a tenth coverage of a full monolayer, the surface diffusion is a determining factor. A rough calculation shows that only an order of millisecond is needed for a SO_2 molecule to reach the FePc site even at the lowest coverage calculated from the equation, $t = \Delta^2/2D_s$, where Δ is the mean square displacement and D_s the surface diffusion coefficient with a typical value of $10^{-11} \text{ cm}^2 \text{ s}^{-1}$. This observation has an important implication for a sensor application in that the amount of the catalyst can be reduced to achieve a maximum activity.

The possibility of a FePc-modified electrode as a SO₂ sensor has been demonstrated by the amperometric detection of SO₂. A concentrated solution of SO₂ was added stepwise to the SO₂-free electrolyte and current was measured where the potential was poised where the SO₂ reduction took place. A linear response was obtained down to ca. 30 ppb (Figure 3), demonstrating that this type of sensor has enough sensitivity for the practical use.

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References and Notes

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