Electrocatalytic Oxidation of Sulfur Dioxide by Iron Phthalocyanine Monolayer in Aqueous Solutions

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The SO_2 oxidation has been paid much attention due to its technological applications in the field of energy production,[1] flue gas desulfurization,[2] and electrowinning of sulfide ores.[3] Most work so far has been done using pure metal, particularly platinum and gold electrodes[4-6] in aqueous solutions. The reactions on these surfaces are highly complicated depending on many factors such as surface pre-treatment, potential range excursed, and the presence of oxides films and thus there is not quite an agreement about the kinetics and mechanisms. Seo and Sawyer[5] suggested that the oxidation of SO_2 proceeds in two steps: one a pure electron transfer process and the other a chemical oxidation by electrolytically formed metal oxides. Lal and coworkers[7,8] reported that SO_2 is reduced *via* an SO intermediate which can be singly- or doubly-bonded to the surface. From studies in concentrated sulfuric acid, Applyby and Pichon[6] suggested SO_2 is oxidized to sulfuric acid *via* the formation of dithionate as a rate-determining step. Recent studies appear to suggest the formation of dithionate ion in weakly acidic to weakly basic solutions. Katagiri and Matsubara suggested[9] that Cu(II) ion catalyzes SO_3^{2-} oxidation to $S_2O_6^{2-}$ *via* the formation of binuclear Cu(II) complex by Raman spectroscopy. From radiotracer study, Vargar *et al.*[10] suggested the oxidation of SO_2 to $S_2O_6^{2-}$ on a gold electrode.

While most researches to date have been carried out on metal surfaces, the electrocatalytic oxidation of SO_2 by adsorbed macrocycles has not been studied to our knowledge. There is only a report on the electrochemical transformation of sulfur oxoanions using water-soluble iron porphyrins.[11]

We have been working on electrocatalytic reactions of NO_x and SO_x using metallo-phthalocyanines. Among them, iron phthalocyanine (FePc) was proven to be particularly effective for NO and SO_2 reduction reactions[12-14] when adsorbed on the surface. The electronic and structural changes upon the surface[15,16] as well as in a sol-gel matrix[17] have also been studied in our group. Based on these previous works, we have tried in this paper the oxidation of SO_2 by the adsorbed FePc monolayer on the electrode surface in aqueous solutions as a function of pH.

Experimental Section

All the chemicals were of analytical grade and used without further purification. The SO_2 concentration was controlled by adding concentrated sodium sulfite solution (1.0 M) to the electrolyte. 18 M deionized water (Millipore Co.) was used to prepare solutions. Adsorption of FePc (Aldrich) onto the edge plane of OPG (ordinary pyrolytic graphite, Union Carbide) was effected by dipping the electrode in a FePc-dissolved DMSO solution. The working electrode was made by molding an OPG piece into the Kel-F plastic and exposing the edge plane. In each experiment, the electrode was ground against 2000-grit SiC paper to ensure the fresh surface.

Electrochemical measurements were performed with a typical three-electrode system and a potentiostat (Autolab PGSTAT 30, ECO CHEM). A Ag | AgCl | KCl(3M) reference and Pt counter electrodes were used. All the measurements were carried out in buffer solutions at room temperature. Buffer solutions in the range of pH 3 to 9 were made using KHP adjusted by H_2SO_4 (pH 3 and 4) and NaOH (pH 5), KH_2PO_4 adjusted by NaOH (pH 6 and 7), and tri(hydroxymethyl)aminomethane adjusted by NaOH (pH 8 and 9). For pH 1 and 2 buffers, sulfuric acid was used and the ionic strength was adjusted by sodium sulfate.

Results and Discussion

Figure 1 shows a series of cyclic voltammograms of SO_2 (2 mM) oxidation by the FePc at different pHs. The coverage of 9.1×10^{-10} mol·cm^{-2} is much larger than that of tetrasulfonated FePc on the basal plane of HOPG (highly oriented pyrolytic graphite). This is due to the rough nature of the edge plane of OPG. Taking the interfacial capacitances of OPG (*ca.* 280 μF·cm^{-2}) and HOPG (*ca.* 3 μF·cm^{-2})[18] into consideration, FePc can be regarded as existing as a monolayer. $[Fe(III)Pc(-2)]^+$, an oxidized form of FePc, exhibits electrocatalytic activities whose peak potential remains constant up to pH *ca.* 4 and shifts negatively by 60 mV per pH (data not shown). Without a FePc layer, no SO_2 oxidation takes place over a wide potential range. The pH-dependence of SO_2 oxidation peak potential does not show a constant variation in accord with FePc redox peak. Most notable is that even with a cathodic scan, the oxidation current is observed in strongly acidic solutions. This is

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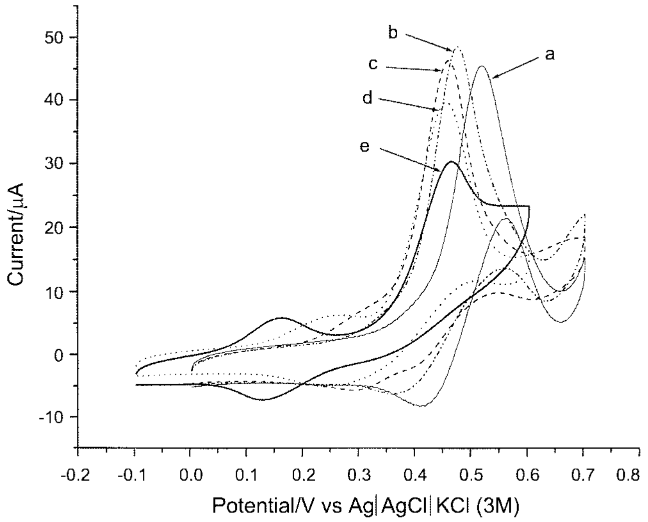

Figure 1. Cyclic voltammetry of SO_2 oxidation by the FePc-adsorbed electrode at pH 1 (a), 2 (b), 3 (c), 5 (d), and 7 (e). C_{SO_2} = 2.0 mM, scan rate = 0.2 $V \cdot s^{-1}$. Apparent electrode area = 0.04 cm^2.

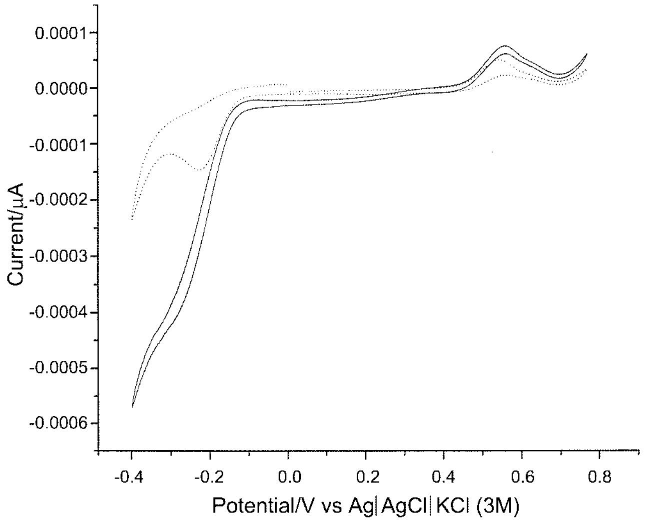

Figure 2. Rotating disk electrode experiments for the SO_2 oxidation and reduction at pH 1 with (solid, 1000 rpm) and without (dotted) rotation. C_{SO_2} = 2.0 mM, scan rate = 0.1 $V \cdot s^{-1}$. Apparent electrode area = 0.1 cm^2.

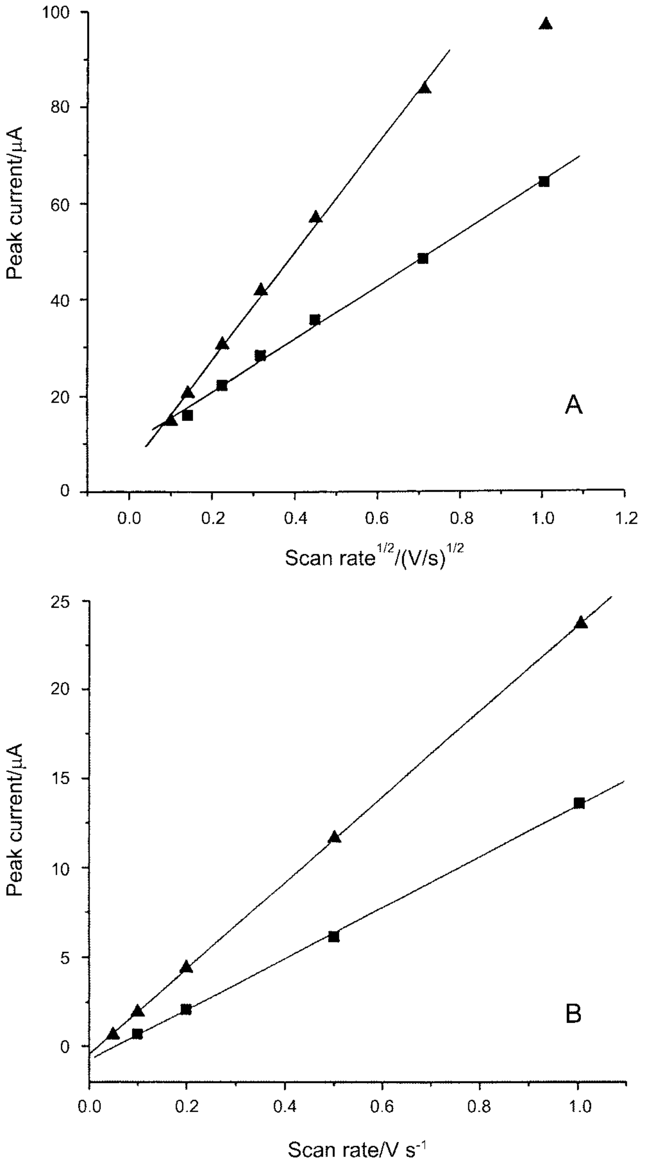

Figure 3. Peak current dependence for FePc-catalyzed SO_2 oxidation on the scan rate. Panel A shows the plot of i_p *vs* $v^{1/2}$ for the peak II at pH 1 (▲) and 5 (■) and Panel B the plot of i_p *vs* v for the peak I at pH 5 (■) and 7 (▲). C_{SO_2} = 2.0 mM. Apparent electrode area = 0.04 cm^2.

characteristic of passivation, implying that the surface is inactivated by the adsorption of an oxidized product of SO_2. As the potential is scanned positively, more and more SO_2 molecules are oxidized and the number of active sites becomes smaller, resulting in the decrease in oxidation current. On the reverse scan, the active site begins to reappear and the oxidation takes place as a result. The fact that the current drop is due to the passivation was confirmed by the experiment with a rotating disk electrode (Figure 2). While a typical sigmoidal shape due to the constant mass transport of SO_2 to the electrode was observed for the reduction, the same current pattern of V-shape was resulted for the oxidation. However, the effect of scanning to the SO_2 reduction region was to decrease the oxidation current due to the formation of sulfur layer over the FePc monolayer. This sulfur layer is formed by disproportionation of sulfoxylic acid ($2H_2SO_2 \rightarrow S + SO_2 + 2H_2O$), which is produced by the SO_2 reduction. This is contrary to the Pt case at which adsorbed sulfur promotes the SO_2 oxidation.[19] The i_p *vs* $v^{1/2}$ plot, where i_p and v are peak current and scan rate, respectively, produces a straight line, indicating that the oxidation process is diffusion-controlled regardless of pH (Panel A, Figure 3). The passivation effect becomes weakened as the solution pH increases and thus SO_2 is simply irreversibly oxidized to sulfate as a final product. The peak current slightly decreases with a pH increase and the oxidation is still observable even at alkaline medium. This is in sharp contrast to the case of SO_2 reduction in that the sulfite ion is not reduced.[14] Three forms of sulfur species, SO_2, HSO_3^-, and SO_3^{2-}, are all electrochemically oxidizable. One of

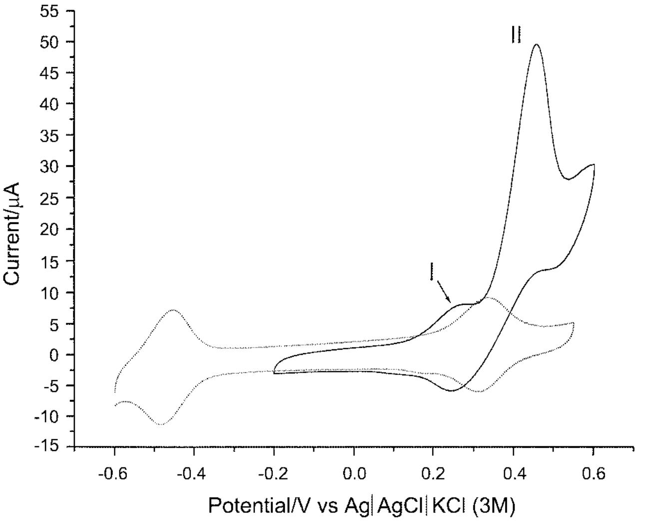

Figure 4. Cyclic voltammetry of the FePc-adsorbed electrode with (solid line) and without (dotted line) SO_2 in a pH 5 solution. C_{SO_2} = 2.0 mM, scan rate = 0.2 $V{\cdot}s^{-1}$. Apparent electrode area = 0.04 cm^2.

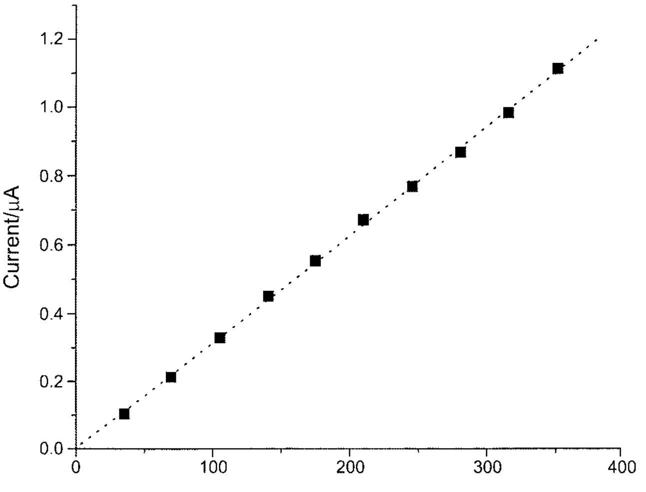

Figure 5. Plot of oxidation current *vs* SO_2 concentration from amperometric experiments in 0.5 M sulfuric acid. The electrode was rotated at 1000 rpm. The potential was held where the maximum oxidation current flows. Apparent electrode area = 0.1 cm^2. R-factor of fit = 0.9996.

reasons for the current decrease could be explained by the decrease in diffusion coefficient for the charged species that can be solvated by the water molecules. The fraction of charged species increases as pH increases.

Above *ca*. pH 3, there begins to appear a small reversible redox pair (peak I, Figure 4) before the main SO_2 oxidation (peak II, Figure 4) takes place. This small peak grows larger as pH increases and still exists even in alkaline solutions. This peak is not due to the oxidation of adsorbed FePc since it appears before Fe(II)Pc(-2) oxidation initiates and is not observable at a low scan rate. We attribute this peak to the oxidation of SO_2 to dithionate ($S_2O_6^{2-}$). Dithionate is known to be very unstable in strongly acidic solutions but becomes stable when the solution is made less acidic. The peak current is directly proportional to the scan rate (Panel B, Figure 3), indicating that dithionate formation is not diffusion-controlled but surface process.

The possibility of a FePc-modified electrode as a SO_2 sensor has been demonstrated by the amperometric detection of SO_2 (Figure 5). A concentrated sulfite solution was added stepwise to the SO_2-free electrolyte and current was measured at a potential where the oxidation occurred while rotating the electrode. A linear response was obtained down to ppb range, demonstrating this type of sensor has enough sensitivity for the practical use.

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