Generation of Superoxide by Adding Polyaniline to Water

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When polyaniline powder was added to water superoxide generated. The formation of superoxide was confirmed by using ESR, amperometry and enzyme techniques.

Superoxide has attracted much attention in the field of biology, because it has been realized that superoxide is produced in biological systems.[1] The radical anion can be also generated artificially, for example, by photochemical reduction of oxygen in the presence of naturally occurring substances such as Chlorophyll.[2] This paper reports that the generation of superoxide by adding the polyaniline powder simply to pure water. The superoxide thus formed was disproportionated into hydrogen peroxide instantaneously.

Polyaniline has also attracted attention as promising material for electrodes of batteries,[3] electric and optical devices,[4] and electrochromic displays.[5] Recent studies revealed that polyaniline acts as a catalyst for oxidation of benzylamine[6] or catechol[7] with oxygen.

Polyaniline was synthesized in a conventional way[8] by oxidative polymerization of aniline with ammonium peroxodisulfate ($(NH_4)_2S_2O_8$) followed by undoping with an aqueous sodium carbonate solution. Doped polyaniline was prepared by further doping with sulfuric acid after polymerization.

Undoped or doped polyaniline was added to pure water with stirring in an atmosphere of air. Generation of superoxide was confirmed by electron spin resonance spectrum (ESR).[9] Since the life time of superoxide is very short and direct detection by ESR spectrometry is difficult, the spin-trap technique was utilized. To 1.5 ml of purified water containing 0.09 M of 5,5-dimethyl-1-Pyrroline-N-oxide (DMPO) as a spin-trap reagent, 0.0255 g of finely powdered undoped polyaniline was added and stirred for 10 min, then after filtration the ESR spectrum was measured. The spectrum is shown in Figure 1. It indicates the presence of an adduct of DMPO and hydroxyl radical (OH•) (adduct A). It has been known that an adduct of DMPO and superoxide converts into adduct A in a few minutes. Since there is possibility that OH• rather than superoxide radical was formed, similar experiments were performed in the presence of either dimethyl sulfoxide (0.5 M) or ethanol (0.5 M). If OH• is present in the solution, spectra of methyl radical or ethanol radical adducts should be observed. Since no changes of the spectra were observed, it was concluded that superoxide was converted into hydroxyl radical. The g-value and coupling constants A_N/mT and A_H/mT for those three spectra were identical at 2.0053, 1.49 and 1.49, respectively.

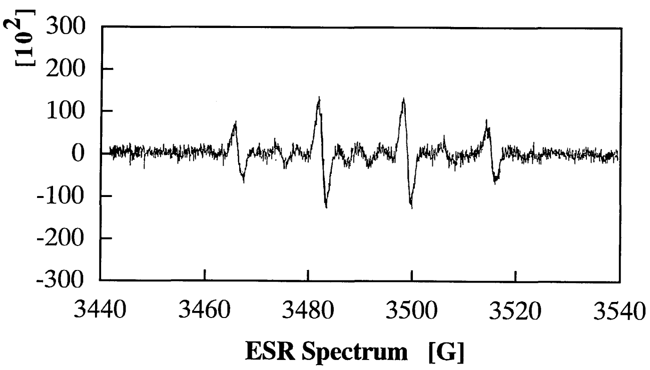

Figure 1. ESR spectrum of an aqueous DMPO solution after the addition of undoped polyaniline powder.

Generation of superoxide was also confirmed by the electrochemical method[10] and enzyme technique.[1] Microhole array electrode (carbon tip with 3.62 x 10^{-4} total electrode area)[11] with 50 μm depth as a working electrode, platinum wire as a counter electrode and SCE as a reference were set in the cell that contains 30 ml of phosphate buffer solution (0.2 M KH_2PO_4 and 0.2 M NaOH) adjusted at pH 7.4. The working electrode was poised at +0.142 V vs. SCE at room temperature. Undoped polyaniline (0.4 g) was added to the cell and stirred. About 80 pA of an oxidation current of superoxide was observed. Then 100 μl of superoxide dismutase (SOD) (25 units in 3.8 M $(NH_4)_2SO_4$ solution, pH 7.0) was added to the solution. The oxidation current completely disappeared. These facts also support the generation of superoxide. The current-time profile is shown in Figure 2. When leucoemeraldine base (the reduced form of polyaniline) (0.4 g) instead of polyaniline was added to the cell, about 1000 pA of the oxidation current was observed.

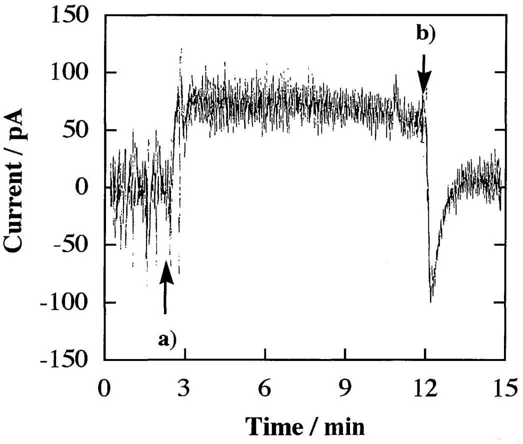

Figure 2. Current-time profile for formation and disappearance of superoxide. **a)** Addition of undoped polyaniline powder in water. **b)** Addition of superoxide dismutase.

The formation of hydrogen peroxide was confirmed by the spectrophotometric method[12] that involves the reaction of titanium(IV) and 8-quinolinol with hydrogen peroxide. The quantitative analysis of hydrogen peroxide was performed by an amperometry using platinized microhole array electrodes in an atmosphere of nitrogen after the addition of an electrolyte. The average absolute values of limiting currents of oxidation and reduction of hydrogen peroxide at +0.9 V and -0.6 V vs. SCE was used for the calculation of the concentration of hydrogen peroxide. The concentration of hydrogen peroxide after 10 min and after 21 h of addition of polyaniline as function of wt% of polyaniline in water is shown in Figure 3. Both doped and undoped polyaniline behaved similarly. The maximum concentration of hydrogen peroxide achieved under the present conditions was about 6 x 10^{-3} wt%. Pure water dissolves 8.1 x 10^{-4} wt% of oxygen at 25 °C. The molar ratio of the produced hydrogen peroxide to polyaniline ranged from 1 x 10^{-4} to 1 x 10^{-3}

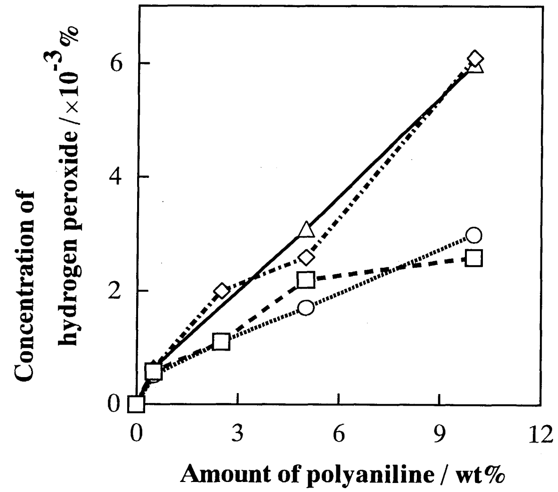

Figure 3. Formation of hydrogen peroxide as function of wt% of polyaniline in water at 25 °C. Undoped polyaniline stirred for 10 min (- -□- -), undoped polyaniline stirred for 21 h (·-·-◇-·-·), doped polyaniline stirred for 10 min (······○······), doped polyaniline stirred for 21 h (——△——).

In order to pursue the behavior of the dissolved oxygen, the reaction was carried out in a closed electrochemical cell that comprised of a 50 ml glass beaker with two platinized microhole arrays, reference and counter electrodes. The cell was filled with 50 ml of phosphate buffer solution adjusted at pH 7.0 and 0.84 g of undoped polyaniline was added at 25 °C with stirring. After about 30 h, the cell was opened to an atmosphere of air. The current-time profile was shown in Figure 4. The currents for hydrogen peroxide were measured at +0.9V, and those for oxygen were calculated from the currents of oxygen at -0.6V by subtracting the value of currents at +0.9V, because the currents at -0.6V include reduction currents for hydrogen peroxide. Oxygen was completely consumed after about 15 h. The amount of hydrogen peroxide produced was smaller than the consumption of oxygen. It is conceivable that hydrogen peroxide decomposed at the diluted condition and/or some superoxide was converted into water. When the cell was opened to air, formation of hydrogen peroxide was observed.

Light seems to not necessary for the reaction, because the hydrogen peroxide formation was observed under the dark conditions.

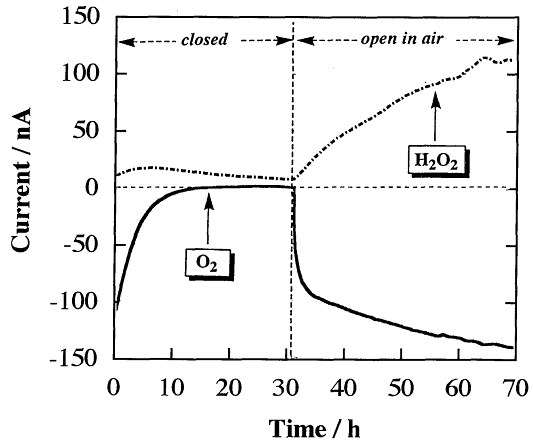

Figure 4. Current-time profile for consumption of oxygen and formation of hydrogen peroxide under the sealed condition. After about 30 h the cell was opened in air.

The structure of polyaniline (emeraldine base) consists of 50% reduced form and 50% oxidized form.[13,14] Since leucoemeraldine base generates larger amount of superoxide, it is conceivable to believe that the reduced part of the structure of polyaniline is responsible for the generation of superoxide.

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