

Photocatalytic Electron and Proton Pumping across Conducting Polymer Films Loaded with Semiconductor Particles

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Polyaniline and polyanion-doped polypyrrole films were demonstrated to have preferential permeability for ions, especially for protons. Transport of electrons and ions through these conducting polymer films was also demonstrated by utilizing the difference of electrochemical potentials of the solutions placed across the films. On the basis of these properties of the conducting polymer films, photocatalytic electron- and proton-pumping systems were constructed, in which conducting polymer films loaded with titanium dioxide or cadmium sulfide particles on one side of the film surfaces were utilized. By photoirradiation of the semiconductor particles, 2-propanol was oxidized on the semiconductor particles and iron-(III) ions were reduced on the other surface of the conducting polymer films. Along with the electrochemical reactions, electrons and ions were cotransported across the conducting films. Protons were concluded to be the chief ionic carrier under the acidic conditions.

Introduction

In the photosynthesis of green plants, proton transport plays an important role. It is involved in the electronic path linking the two photosystems and is utilized for producing a difference in the chemical potentials across the thylakoid membrane as the pH difference.¹ These functions will also be essential to the construction of artificial photosynthetic systems. We, therefore, have studied artificial proton pumping systems with a view to constructing new energy conversion systems. So far, we have succeeded in constructing two kinds of prototypes of the systems. One system utilizes redox reactions of a quinone derivative on the platinum-loaded Nafion electrodes at oil/water boundaries,² and the other system utilizes redox reactions of a pair of conducting polymer electrodes.³ Both systems operate with the electric energy supplied externally.

In the next stage of these studies, we have intended to develop systems working photochemically. For this purpose, in the present study, we surveyed the functions of conducting polymer films loaded with semiconductor particles. Such composite films attracted our interests for the following reasons. First, the flexible molecular structure of the polymers is suited for fixing the photocatalyst particles on the surface.⁴ Second, the electronic and ionic conductivity of the conducting polymers

is expected to be utilized for the operation of the systems. Third, the films can separate solutions with different chemical potentials and pH's at both sides of the films.

Conducting polymers incorporate and release ionic species repeatedly as the result of their redox reactions. This means that protons and other ions can penetrate into the conducting polymers.^{5–7} In the first step of the present work, we studied the proton permeability in the conducting polymer films. In the next step, we surveyed the electron and ion transport, which is driven by utilizing the redox potential difference of the solutions placed at both sides of the films. In the final step, we constructed an electron and proton pumping system driven by the photocatalytic reactions.

Experimental Section

Materials. Polyaniline soluble in *N*-methylpyrrolidone was synthesized chemically according to the literature.⁸ The films of polyaniline were obtained by casting the solution on a glass plate. The films were made electrically conductive by immersing them in sulfuric acid solution. The chemical structure at the conductive state is shown in Figure 1a. Polypyrrole films were supplied by Ciba-Geigy Japan. They were synthesized electrochemically. Their chemical structure is shown in Figure 1b. The dopant of the films was solely the polyanion, whose number-average and mass-average molecular masses were 13 700 and 49 000, respectively. Compared with the conventional polypyrrole, the polyanion-doped polypyrrole films have much improved mechanical strength and thermal plasticity

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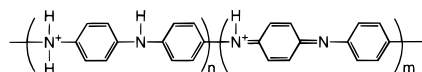
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(a) Polyaniline



(b) Polypyrrole

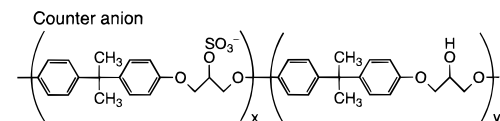
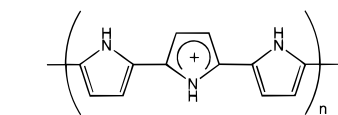


Figure 1. Chemical structure of conducting polyaniline (a) and polypyrrole having polyanion as the dopant (b).

because of the properties of the doped polyanion.^{9,10}

Titanium dioxide (TiO₂) and cadmium sulfide (CdS) powders were commercially obtained from Kanto Chemical Co., Inc., and Furuuchi Chemical Co., Inc., respectively. Both were guaranteed reagents and used without further purification. For the colorimetry of iron(II) ions, 2,4,6-tris(2-pyridyl)-s-triazine obtained from Dojindo Laboratories was used as the complexing reagent. Other chemicals were purchased from commercial sources as guaranteed reagents and used without further purification.

Electron- and Proton-Transport Experiments. The polypyrrole and polyaniline films were mechanically strong and free from pinholes, when they were thicker than 10 μm . They were fixed in the electrochemical cells shown in Figure 2 as the separator of the two compartments. Fluorocarbon rubber seals were used to tighten the films. The area of the films exposed to the solution at both sides was 2.8 cm² each.

For the purpose of transporting electrons and protons photocatalytically, composite films were fabricated using the conducting polymer films with thicknesses of about 10 μm and semiconductor particles. In the case of the polypyrrole films, the semiconductor particles were loaded by pressing the particles on one side of the film faces at 140 $^{\circ}\text{C}$ under the pressure of 1.0 MPa. For making polyaniline films loaded with semiconductor particles, 0.1 g of the semiconductor powder was added to 2.0 g of the solution of polyaniline dissolved in 1-methyl-2-pyrrolidone at 5 wt %. This suspension was cast on a glass plate, and the cast films were dried in a vacuum oven at 50 $^{\circ}\text{C}$. During the procedure, the semiconductor particles sank in the wet polyaniline films and were deposited on the bottom surface of the films.

Electrochemical measurements were carried out using a Nikko-Keisoku potentiostat NPOT-2501 and a Nikko-Keisoku digital Coulomb meter NDCM-3. A TOA HM-60S pH meter equipped with a TOA GSH-531c combined electrode was used for pH measurements after calibration with appropriate standard aqueous buffers. Absorption spectra were recorded with a Shimadzu UV-360 spectrophotometer.

For photoirradiation, a 500 W high-pressure Hg lamp (Wacom R&D Corp., BMO-500DI) and a 500 W Xe lamp (Wacom R&D Corp., KXL-500F) were used as the light sources. The light beams were passed through a 1-cm water filter and a soda-lime glass plate to cut off the heat and UV radiation.

Results and Discussion

Permeability of Protons in the Conducting Polymer Films. We have already reported the permeability of protons in the polyanion-doped polypyrrole film.³ In the present study, the permeability of protons in the

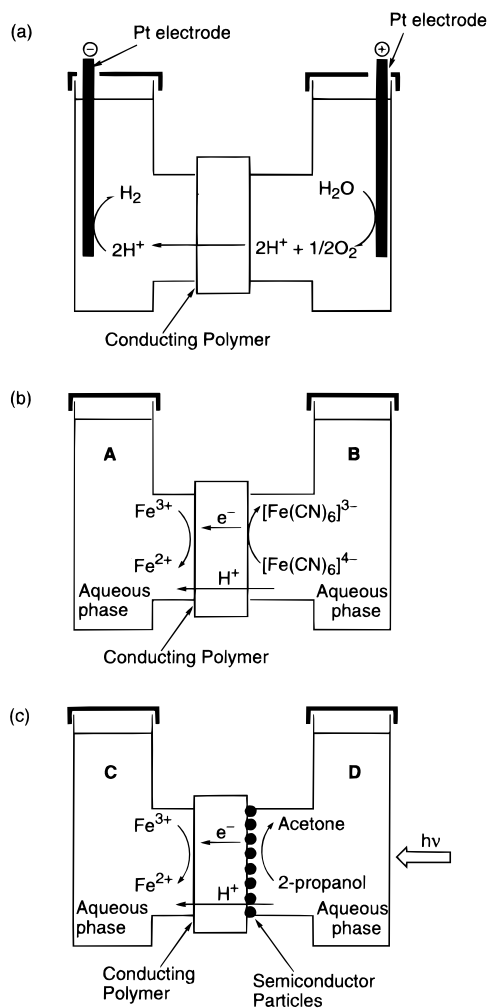


Figure 2. Experimental setups for the measurement of electron and ion transport through the conducting polymer films; (a) for the ion permeability, (b) for the electron and ion transport driven by chemical potential difference across the conducting polymer film, and (c) for the electron and ion transport driven by the photoirradiation of semiconductor particles loaded on one side of the film.

polyaniline and polypyrrole films was comparatively studied using the two-compartment cell as shown in Figure 2a. The solution in the cell contained sodium sulfate (0.2 mol dm⁻³) as the supporting electrolyte. The pH was adjusted at 3 by adding an aqueous solution of sulfuric acid, because polyaniline films are electrically conducting in acidic conditions.¹¹ Electrochemical measurements were carried out after the conducting films were equilibrated with the solution. When voltages higher than about 1.7 V were applied between the two platinum electrodes across the conducting polymer films, continuous currents began to flow between the electrodes. As the current flows, ionic species are transported through the conducting polymer films to maintain the electric neutrality of the solutions of the two compartments. If the protons are the sole ionic species mobile in the conducting polymers, no pH changes are to be observed by the electrolysis. This is because the protons generated and consumed by the electrochemical reactions on the platinum electrodes are compensated by the protons transported through the

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films. In the experiments, we observed the small changes in the pH of the solutions after passing the current. Typically, current at the density of 1 mA cm^{-2} was passed through the polyaniline film for about 1 h until the total charge reached 10 C. From the comparison of the pH changes and the electric charges passed as the current, protons transported across the films were determined to be 87 and 90% of the ionic species passed through the polypyrrole and polyaniline films, respectively. Since the concentration of protons in the solution was about 1/500 of other ionic species in the solution, the conducting polymer films are concluded to have higher permeability for protons than for other ionic species.

From the analysis of the current–voltage characteristic of the electrolysis in the acidic solution in the above cell, the electric resistance for the proton conduction through the polyaniline and polypyrrole films about $10 \text{ }\mu\text{m}$ thick was evaluated to be about 1.2 and $640 \text{ k}\Omega \text{ cm}^{-2}$, respectively. The resistance of the polyaniline and polypyrrole films increased with the film thickness. The lower resistivity for the polyaniline films than for the polypyrrole films is probably due the protonic acid included in the polyaniline films,¹¹ especially in the electrically conducting conditions.

Electron and Ion Transfer Driven by the Difference in the Redox Potentials of the Solutions at Both Sides of the Conducting Polymer Films. On the basis of the experimental results on the proton transport through the conducting polymers, we studied the chemically driven electron and proton transport through the films in the cell shown by Figure 2b. Although the purpose is different from ours, Lawson et al. have studied the concerted electron and anion transport through polypyrrole, which was embedded in a microporous membrane.⁵ Contrary to their system, our polypyrrole films have the permeability to cations because they are doped with the polyanions.

In our study the measurements were carried out in the two-compartment cell containing solutions with different chemical potentials, as shown in Figure 2b. The pH of the solution was adjusted at 2.0, so that polyaniline showed high conductivity.¹¹ Typical procedures of the measurements and the results obtained using the polyaniline films are as follows. First, potassium hexacyanoferrate(II) ($4.6 \times 10^{-3} \text{ mol dm}^{-3}$) was added to the solution of compartment B. The solution showed a slight spectral change due to the redox reactions between the solution and the polyaniline film. After the spectral change stopped, iron(III) chloride ($2.5 \times 10^{-2} \text{ mol dm}^{-3}$) was added to compartment A. By the addition, continuous spectral changes in the solution of compartment B started owing to the oxidation of hexacyanoferrate(II) ions. The time course of the increase of the concentration of hexacyanoferrate(III) ions is shown in Figure 3. From the colorimetric analysis, the increase of iron(II) ions in compartment A was also detected. The rates of the increase of the concentrations of hexacyanoferrate(III) and iron(II) ions agreed well. The increase of the concentration of iron(II) ions in compartment A was also observed by adding potassium iodide (0.15 mol dm^{-3}) or hydroquinone (0.01 mol dm^{-3}) to the solution of compartment B.

The above results indicate that iron(III) ions oxidize hexacyanoferrate(II) ions, iodide ions, and hydroquinone

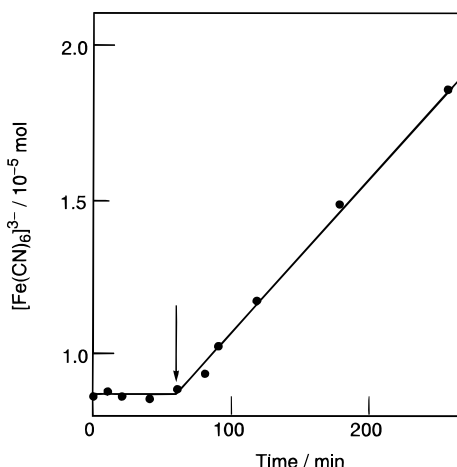


Figure 3. Time course of the conversion of hexacyanoferrate(II) ions into hexacyanoferrate(III) ions as the result of the redox reactions in the cell as shown in Figure 2b, in which a polyaniline film was used as the separator. Initially, potassium hexacyanoferrate(II) was added to compartment B (100 mL) at the concentration of $4.6 \times 10^{-3} \text{ mol dm}^{-3}$. The arrow indicates the time when iron(III) chloride was added to compartment A (100 mL) at the concentration of $0.025 \text{ mol dm}^{-3}$.

through the polyaniline film. This, in turn, indicates that ionic species are also transported between compartments A and B through the polyaniline film to keep the electric neutrality of the solutions. Unfortunately, we failed the determination of the amount of protons transported between the two solutions as the change of pH because of the slow reaction rate and the low pH (pH 2.0) of the solutions. However, most of the transported ionic species under the present conditions are attributable to protons on the basis of the experimental results obtained in the previous section; the experiments of the previous section were carried out at the proton concentration lower by 1 order than the present experiments.

When we used polypyrrole instead of polyaniline as the conducting polymer film, no reaction proceeded by the addition of the iron(III) ions and reductants to compartments A and B, respectively. This result suggests that the relationship between the energy levels of conducting polymers and the redox potentials of solutions is important to forward the reactions. Since the conducting polymers used in this study had the oxidized forms at the conducting state, the requisite for forwarding the reaction at the interface with compartment B is that the conducting polymers can be reduced by the reductants. The electrochemical reduction of the polyaniline and polyanion-doped polypyrrole were observed at the potentials negative of +0.77 and +0.07 V vs NHE in the solution at pH 2.0. The reduction of polyaniline and polypyrrole films at similar potentials has been reported.¹² The redox potentials of the compounds used in the present experiments are as follows: hexacyanoferrate(III)/hexacyanoferrate(II) = 0.36, benzoquinone/hydroquinone = 0.46 at pH 2.0, $\text{I}_3^-/\text{I}^- = 0.54$, iron(III)/iron(II) = 0.77. The energetic relationship among the substances suggests that it is difficult to reduce the polypyrrole film by these reductants. This is in good agreement with the experimental results that

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the redox reactions were not observed across the polypyrrole films.

On the basis of the above results, the following mechanism can be deduced for the transport of electrons and protons through the polyaniline films. In the first step of the reaction, the electrons are transferred from the reductant in compartment B to polyaniline. As the result, polyaniline is partly reduced and ions are exchanged between polyaniline and the solution in compartment B to neutralize the negative charge due to the injected electrons. In the next step, electrons are transferred from the polyaniline films to iron(III) ions in compartment A to form iron(II) ions, when iron(III) is introduced into compartment A. By this process, polyaniline film is reoxidized and ionic species are exchanged between polyaniline and the solution in compartment A. In the stationary state, these reactions occur at both sides of the film. Experimental results tell us that protons have high mobility in the polyaniline film, probably because of their small size. Hence, the electrons and protons are expected to be transported continuously from compartment B to compartment A at the stationary state, when the experiments are carried out under the acidic conditions.

The conditions of the films at the stationary state are not necessarily identical with those of the electrochemically reduced and oxidized states of the conducting polymers. For example, the polyaniline films at the stationary state probably have the depth profile of the oxidized states different from the films under the electrochemically controlled conditions. The mechanisms of the ion transport through the films and the electrochemical doping and undoping processes are not expected to be the same. The depth profile of the oxidized states and the detailed mechanism of the transport of electrons, ions, and protons will be elucidated, when the microscopic structure and chemical states of the conducting polymers across the films are fully understood.

Photocatalytic Electron and Proton Transport Using Conducting Polymer Films Loaded with Semiconductor Particles. Photoexcitation of semiconductor particles produces electrons and holes in the conduction and valence bands, respectively. They react with the compounds on the semiconductor particles to produce reduced and oxidized substances. These reactions provide the means of converting light energy into chemical energy and treating harmful substances.¹³ It has also been reported that the polyaniline films homogeneously mixed with TiO₂ particles show the photochromic properties, when irradiated in the presence of ethanol.¹⁴ For the conversion of light energy using semiconductor particles, however, the back reactions between the products are the problem. In the study of this section, we used the conducting polymer films loaded with semiconductor particles on one surface to prevent the problem. Oxidation reactions are expected to take place on the n-type semiconductor particles such as titanium dioxide, and reduction reactions on the opposite surface of the films. Owing to the asymmetric structure, the back reactions are expected to be much prevented.

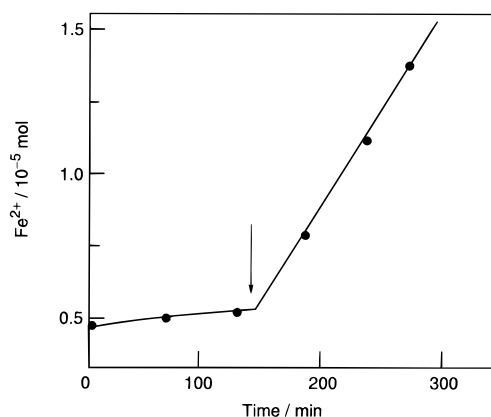


Figure 4. Time course of the conversion of iron(III) ions into iron(II) ions by the photoirradiation of cadmium sulfide particles loaded on polypyrrole film in the cell shown in Figure 2c. Initially, compartments C and D contained 100-mL aqueous solutions of iron(III) chloride ($4.9 \times 10^{-2} \text{ mol dm}^{-3}$) and 2-propanol (0.39 mol dm^{-3}), respectively. The arrow indicates the time when the photoirradiation started.

The composite films were obtained by loading titanium dioxide or cadmium sulfide particles on one side of the conducting polymer films. The details of the loading methods are described in the experimental section. Using the composite films, the photocatalytic electron and proton transport experiments were carried out in the cell shown schematically in Figure 2c. Compartments C and D contained aqueous solution of iron(III) chloride ($4.9 \times 10^{-2} \text{ mol dm}^{-3}$) and aqueous solution of 2-propanol ($3.9 \times 10^{-1} \text{ mol dm}^{-3}$), respectively. The semiconductor-loaded side of the conduction polymer films faced the solution of 2-propanol. By photoirradiation of the semiconductor particles, 2-propanol is oxidized into acetone on the semiconductor particles.¹⁵ This reaction leaves electrons in the semiconductor particles. The electrons are then transferred into the conducting polymers, because the potentials of the conduction bands of cadmium sulfide¹⁶ and titanium dioxide^{13,17} are negative enough to reduce the conducting polymers. Once the electrons are transferred to the conducting polymers, the situation is the same as the experiments of chemically driven electron and ion transport. Namely, it is expected that the reduced conducting polymer transfers the electron to the iron(III) ions in compartment C. To maintain the electric neutrality, it is also expected that ions are transported through the conduction polymer films. In the acidic solutions the protons are assumed to be the chief ionic species transported because of the high permeability of the conducting polymers to protons.

Figure 4 shows that the concentration of iron(II) ions in compartment C increases by the photoirradiation of cadmium sulfide loaded on the polyaniline film. The slope of Figure 4 gives the reaction rate of $3.8 \times 10^{-6} \text{ mol h}^{-1}$ under the irradiation of the light from a 500 W xenon lamp. Similar results were obtained using the titanium dioxide-loaded polyaniline film, when irradiated by a 500 W high-pressure Hg lamp.

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Table 1. Rates of the Photocatalytic Reactions through the Semiconductor-Loaded Conducting Polymer Films^a

photocatalyst	conducting polymer	reaction rate/ 10^{-6} mol h ⁻¹
TiO ₂	polyaniline	2.7
TiO ₂	polypyrrole	0.34
CdS	polyaniline	3.8
CdS	polypyrrole	0.26

^a Measurements were carried out in the cell shown in Figure 2c. The cell contained aqueous solutions of iron(III) chloride (4.9×10^{-2} mol dm⁻³) in compartment C (100 mL) and 2-propanol (0.39 mol dm⁻³) in compartment D (100 mL).

The increase of iron(II) ions in compartment C was also observed when the polypyrrole films loaded with cadmium sulfide or titanium dioxide were irradiated. Since the reactions did not proceed across the polypyrrole films by the chemically driven system as described in the previous section, this result indicates that the photoirradiated semiconductor particles have stronger reducing power than the reductants.

The results obtained using the composite films are summarized in Table 1. Polyaniline films show the reaction rates about 1 order of magnitude higher than polypyrrole films. The difference in the reaction rates is probably due to the difference in their resistivity for the ion transport; the lower resistivity is estimated for the polyaniline films by the electrochemical measurements as described previously.

Part of the holes photogenerated in the semiconductor particles may be transferred to the conducting polymers and not only to the chemicals in solution or 2-propanol. If the holes are transported to the conducting polymers, they consume part of the electrons injected from the photoirradiated semiconductor particles, leading to the lowering of the net reaction rates. More seriously, conducting polymers are sometimes deteriorated oxidatively, if excessive amounts of holes are transferred. Generally, this is serious when titanium dioxide is used as the photocatalyst, because the positive holes formed

in it has very strong oxidizing power. In our study, however, the reaction rate was constant over 12 h for the irradiation of the titanium dioxide-loaded conducting polymer films. This probably means that 2-propanol reacts very rapidly with the positive holes in titanium dioxide loaded on the conducting polymer films.

Conclusion

On the basis of the experimental results, we have demonstrated that electrons are transported across the conducting polymer films as the result of the photocatalytic reactions on the semiconductor particles loaded on the conducting polymer films. To maintain the electric neutrality of the solutions ionic species are also transported across the films. Most of the ionic species transported under the acidic conditions are attributed to protons. Although the pH changes were not detected under the experimental conditions, the system is therefore regarded as the light-driven proton pump. To make a measurable pH difference across the conducting polymer films in the acidic conditions, the selectivity for the permeation of protons should be increased further. Energetically, the chemical reactions demonstrated in the present work are exothermic, and the light is utilized only to open the reaction channel. However, this system has the meaning in that the vectorial transport of electrons and ions is realized photocatalytically. By introducing semiconductor particles on the other side of the conducting polymer films, the linkage of two photocatalytic reaction systems and the construction of an artificial Z-scheme of photosynthesis will be attainable.

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