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POLYMERIZATION OF TRANSITION METAL COMPLEXES IN SOLID POLYMER ELECTROLYTE MEMBRANES

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ABSTRACT

Prussian blue (PB), which is a mixed-valent polynuclear metal complex, was formed in the presence of the solid polymer electrolyte membrane Nafion (Nf). According to the stepwise dipping method, in which either Fe^{2+} or $Fe(CN)_6{}^{3-}$ of the component ions of PB was first incorporated into the matrix membrane and then the membrane was immersed into a solution containing the other component ion, a thin layer of PB was deposited on the surface of Nf or inside Nf depending upon the sequence of incorporation of the component ions. A dissipative structure of periodic PB layer deposit inside Nf was found to be formed under a specific condition of the stepwise method. PB was also formed inside Nf as a broader line by the countercurrent diffusion method in which both component ions were incorporated into Nf from opposite surfaces. The position of PB in Nf varied with the concentration ratio of Fe^{2+} to $Fe(CN)_6{}^{3-}$ in this case.

1. INTRODUCTION

Considerable attention is being paid to ultrafine particle-dispersing membranes in which platinum colloid [1], cadmium sulfide [2, 3], polypyrrole [4-6], silver halides [7, 8], and other functional particles [9, 10] are impregnated in solid polymer films by means of chemical or electrochemical procedures. A solid-phase technique for the preparation of ultrafine particles

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in polymer films is attractive among the several different methods reported to date, since it has the following advantages in manufacturing functional materials: 1) It efficiently carries out the dispersion of ultrafine particles without aggregation in a solid film, while it is not easy to achieve this in solution by other methods; and 2) such processes as film-casting and solvent-evaporation are not required in this process, as they generally are in conventional methods. We have found a similar solid-phase technique for thin-film preparation of polynuclear transition metal complexes, such as Prussian blue (PB) and Magnus green salt (MGS), on a solid matrix of a Nafion (Nf) membrane [11]. It has been difficult to process this sort of polymeric metal complex as a thin film or a fine particle because of the minimal solubility and/or poor processability. Our method has overcome this problem and a new way has been found for the production of solid-state electrochemical devices [12]. In this paper, correlations between membrane structure and reaction conditions for the PB complexation in Nf will be described.

2. EXPERIMENTAL

(2-1) PB Formation on the Surface of Nf by the Stepwise Method

Nafion 117 produced by Du Pont (perfluorinated cation exchange membrane, approximately 200 μm in thickness) was used for all experiments reported here. All Nf membranes were cleaned by boiling in concentrated HNO_3 and then sufficiently washed with boiling distilled water.

A piece of cleaned Nf (1×1 cm^2) was immersed in 10 mM (M = mol/dm^3) $FeCl_2$ aqueous solution for 10 min under argon and then dried in a desiccator under reduced pressure for about 5 min. The membrane was then immersed in an aqueous $K_3Fe(CN)_6$ solution (1-500 mM) without stirring. The resulting blue membrane was washed sufficiently with distilled water in order to remove unreacted $K_3Fe(CN)_6$.

(2-2) PB Formation inside Nf by Stepwise Method

A piece of Nf (1×1 cm^2) was placed in an aqueous $K_3Fe(CN)_6$ solution (10-1000 mM) and an aqueous $FeCl_2$ solution (1-8000 mM), successively, for 60 min in each solution without stirring. Not stirring the solution was important in order to make the PB precipitation homogeneous, but the solutions were stirred when the concentrations of the component ions were extremely low, because then PB formation was too slow without stirring.

(2-3) PB Formation inside Nf by Countercurrent Diffusion Method

PB was precipitated inside Nf according to the countercurrent diffusion method as described in a previous paper [8] as follows: The Nf membrane was placed between two compartments of a separable cell, in one compartment of which was placed 2 m*M* aqueous $FeCl_2$ solution and in the other compartment of which was placed an aqueous $K_3Fe(CN)_6$ solution (20-2000 m*M*). Both of the component ions of PB were thus incorporated into the Nf by countercurrent diffusion, encountering each other inside the membrane, so that PB was precipitated inside the Nf. The membrane was taken out of the cell 2 min after the complexation and then washed with distilled water.

(2-4) Structural Analyses of the PB/Nf Composite Membranes

The PB deposition on the surface of Nf was quantitatively followed by using a UV-visible absorption spectrometer (Model UV-210 A, Shimadzu Co.), in which the sample was sandwiched between two plates of glass to measure the optical density at 650 nm at various intervals of complexation time. The PB/Nf membrane was sliced to a thin film with a razor blade to observe the structure of a cross section of the PB/Nf composite using a scanning electron microscope (Model S-800, Hitachi Co.) and an optical microscope (Model XF-11, Nihonkogaku Co.). The iron distribution in the cross section of the PB/Nf membranes was determined by using an electron probe microanalyzer (Model EPM-810, Shimadzu Co.), where the membranes were sufficiently washed with 1 *M* aqueous KCl solution for a couple of days by changing the KCl solution twice a day in order to completely remove unreacted Fe^{2+} and/or $Fe(CN)_6{}^{3-}$ ions from the matrix membrane.

3. RESULTS AND DISCUSSION

(3-1) General Aspects on PB Formation in Nf Membrane

If one of the two component ions of PB, Fe^{2+} or $Fe(CN)_6{}^{3-}$, was incorporated into Nf and then the resulting membrane was immersed in an aqueous solution containing the other component ion, the insoluble PB particles were formed on the surface of or inside the matrix at the place where the component ions encountered each other. For example, when Fe^{2+} was first incorporated into Nf, PB precipitated on the surface, as indicated in Fig. 1(A). In contrast, PB precipitated inside Nf when $Fe(CN)_6{}^{3-}$ was first introduced into

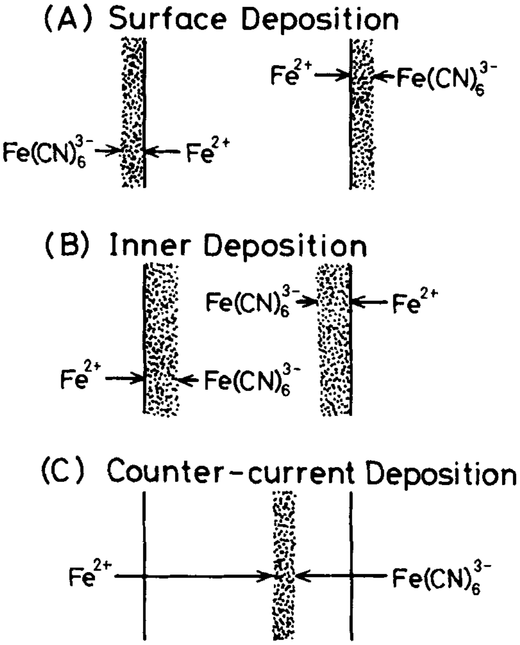

FIG. 1. Correlation of preparation procedure to membrane structure for the PB formation in Nf solid film. Processes (A) and (B) are stepwise incorporations of the component ions Fe^{2+} and $Fe(CN)_6{}^{3-}$ in Nf, and Process (C) is a countercurrent diffusion incorporation.

Nf prior to complexation with Fe^{2+}. In the latter case, PB layers were generally split into two as shown in Fig. 1(B), although it was basically possible to disperse PB particles homogeneously in Nf depending on the concentrations of the two component ions.

If Fe^{2+} and $Fe(CN)_6{}^{3-}$ were incorporated into Nf from opposite surfaces in a countercurrent diffusion way, PB was formed as one band inside the Nf. It was hereby possible to deposit PB at any arbitrary position in the matrix by controlling the concentration and a direction of diffusion of each component ion.

In addition, when Fe^{3+} was bound to Nf for the complexation with $Fe(CN)_6{}^{4-}$, PB formation did not, however, proceed uniformly and efficiently although PB is known to be obtained in water by mixing either Fe^{2+} and $Fe(CN)_6{}^{3-}$ or Fe^{3+} and $Fe(CN)_6{}^{4-}$. Fe^{3+} is considered to interact more strongly with the sulfonate groups of Nf than Fe^{2+} due to the higher positive charge of the ion. That might retard the diffusion of Fe^{3+} in the Nf, so that the PB formation was not taking place so efficiently in this case as for the complexation of Fe^{2+} with $Fe(CN)_6{}^{3-}$.

(3-2) Surface Deposition of PB on Nf

Figure 2 shows the change in the visible absorption with time at an early stage of the PB formation on Nf when Nf was immersed in 10 m*M* $FeCl_2$ for 10 min and then in 100 m*M* $K_3Fe(CN)_6$. An Fe^{2+}-adsorbing yellowish membrane turned blue immediately after being immersed in ferricyanide solution. An absorption peak, at the beginning around 750 nm, shifted toward shorter wavelengths and finally reached 700 nm and stayed there with increasing optical density. A species absorbing at 700 nm could be identified with the PB complex itself as prepared by the electrochemical method [13, 14]. The absorption maximum at longer wavelengths is considered to be assignable to a species that has a somewhat different chemical composition from that of the so-called PB. Actually, PB colloid prepared in water by mixing $FeCl_2$ and $K_3Fe(CN)_6$ in a large excess of Fe^{2+} to $Fe(CN)_6{}^{3-}$ had an absorption maximum at a wavelength longer than 700 nm, while PB colloid prepared at an equimolar ratio had an absorption maximum at exactly 700 nm. The complexation in Nf in the early stage would take place when Fe^{2+} was in a large excess over $Fe(CN)_6{}^{3-}$ in the Nf, thus explaining why the absorption peak was initially at a longer wavelength.

Figure 3 shows the time dependence of the PB formation on the Nf surface at different concentrations of $K_3Fe(CN)_6$. PB formation seems to take place in a biphasic way. Considering the time scale of each elementary step of this figure, it might be said that the initial stage corresponds to the process accompanying the spectral change (blue shift) shown in Fig. 2. Figure 4 shows SEM pictures of the surfaces of the PB/Nf composite membranes which were obtained at early and later stages of the complexation. The PB complex deposited on Nf had an amorphous structure at the early stage and changed to a cubic crystalline form on aging. The PB formation in the solid matrix thus proceeds with changes of chemical and morphological structure to reach a final form of the so-called Prussian blue.

It was uncertain why the PB growth was faster for 30 m*M* than for 100 m*M* $K_3Fe(CN)_6$ solution, as shown in Fig. 3. The growth rate was found to be maximum around 30 m*M* $K_3Fe(CN)_6$ and to decrease rapidly with increasing the concentration above this point. It might be due to some factors governing solution properties such as ionic strength and viscosity or to some redox re-

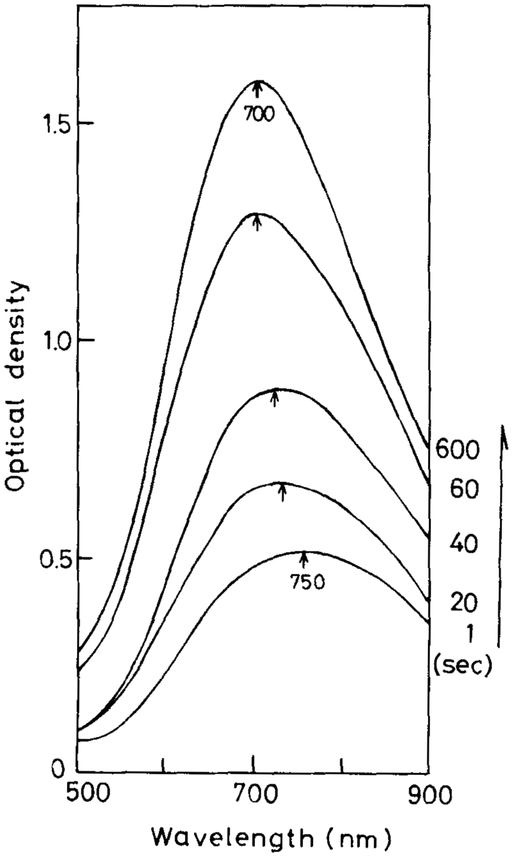

FIG. 2. Visible absorption spectral change of the PB formation on the surface of Nf. Nf was immersed in 10 m*M* $FeCl_2$ for 10 min prior to the complexation with $K_3Fe(CN)_6$. Numbers on the right ordinate are the length of time of immersing Nf in $K_3Fe(CN)_6$ solution.

actions of PB formed on the Nf surface with $Fe(CN)_6{}^{3-}$ and/or other reducing species.

(3-3) Periodical Precipitation of PB in Nf

As mentioned previously, a PB layer was formed inside Nf when $Fe(CN)_6{}^{3-}$ was introduced into Nf prior to Fe^{2+}. If the concentration of Fe^{2+} was higher

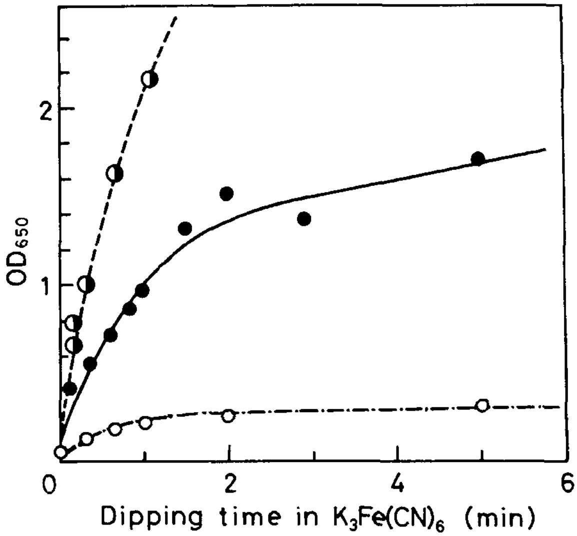

FIG. 3. PB growth curves for surface deposition at different concentrations of $K_3Fe(CN)_6$. Nf was immersed in 10 m*M* $FeCl_2$ for 10 min and then placed in $K_3Fe(CN)_6$ solution at different concentrations. (○) 1 m*M*, (◐) 30 m*M*, (●) 100 m*M*.

than 4-5 *M*, PB homogeneously precipitated inside the Nf. If the concentration was lower than that, PB was generally split into two layers. That is, there was no PB at the center of Nf membrane. It was difficult to determine specific boundary conditions between the homogeneous and split structures in terms of the concentrations of $FeCl_2$ and $K_3Fe(CN)_6$ as there was an intermediate zone where the resulting structure varied from the homogeneous to split one depending on some uncertain factors, such as stirring of solution, shape and thickness of the membrane, etc.

In any event, interestingly, the PB was split into 7-8 layers in a periodical pattern, as shown in Fig. 5, under a certain combination of the concentrations of two component ions, Fe^{2+} and $Fe(CN)_6{}^{3-}$. It was, however, also difficult to fix the specific concentrations although it could be safely said that this occurred when the concentration of $FeCl_2$ was much lower than that of $K_3Fe(CN)_6$, e.g., $FeCl_2 < 10$ m*M* and $K_3Fe(CN)_6$ 300-500 m*M*. Similar findings have also been reported for the precipitation of silver halides in solid thin films of poly(vinyl alcohol) [7] and Nafion [8]. These are basically the same in appearance

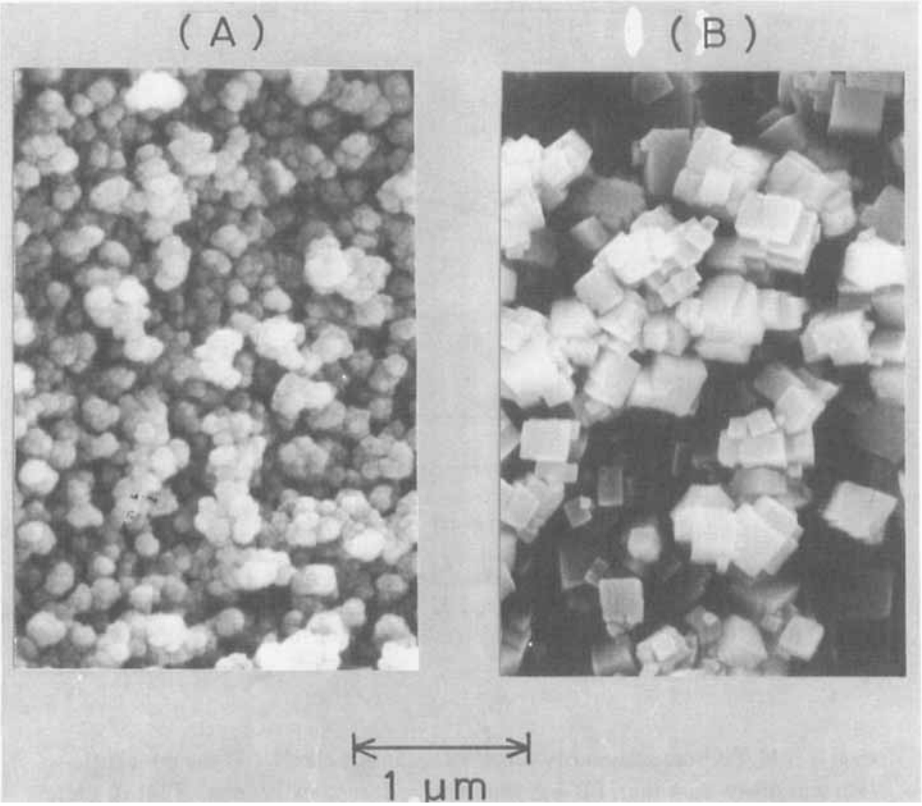

FIG. 4. SEM pictures of the surface-deposition type of PB-Nf composite membrane at early (A) and later (B) stage of the complexation. Nf was immersed in 100 m*M* $K_3Fe(CN)_6$ for 1 min (A) and for 20 h (B), respectively, after immersion in 10 m*M* $FeCl_2$ for 10 min.

as the Liesegang phenomenon, well known in gels. Studies of dense polymer films have been less extensive than of gels, but they are more appropriate in view of applications for new kinds of multilayered materials which might be useful as light modulators because of birefringence in polarized light.

(3-4) Countercurrent Deposition of PB in Nf

It was important in the countercurrent diffusion method to set the concentration of $K_3Fe(CN)_6$ higher than that of $FeCl_2$ by a factor of 10-500 in order

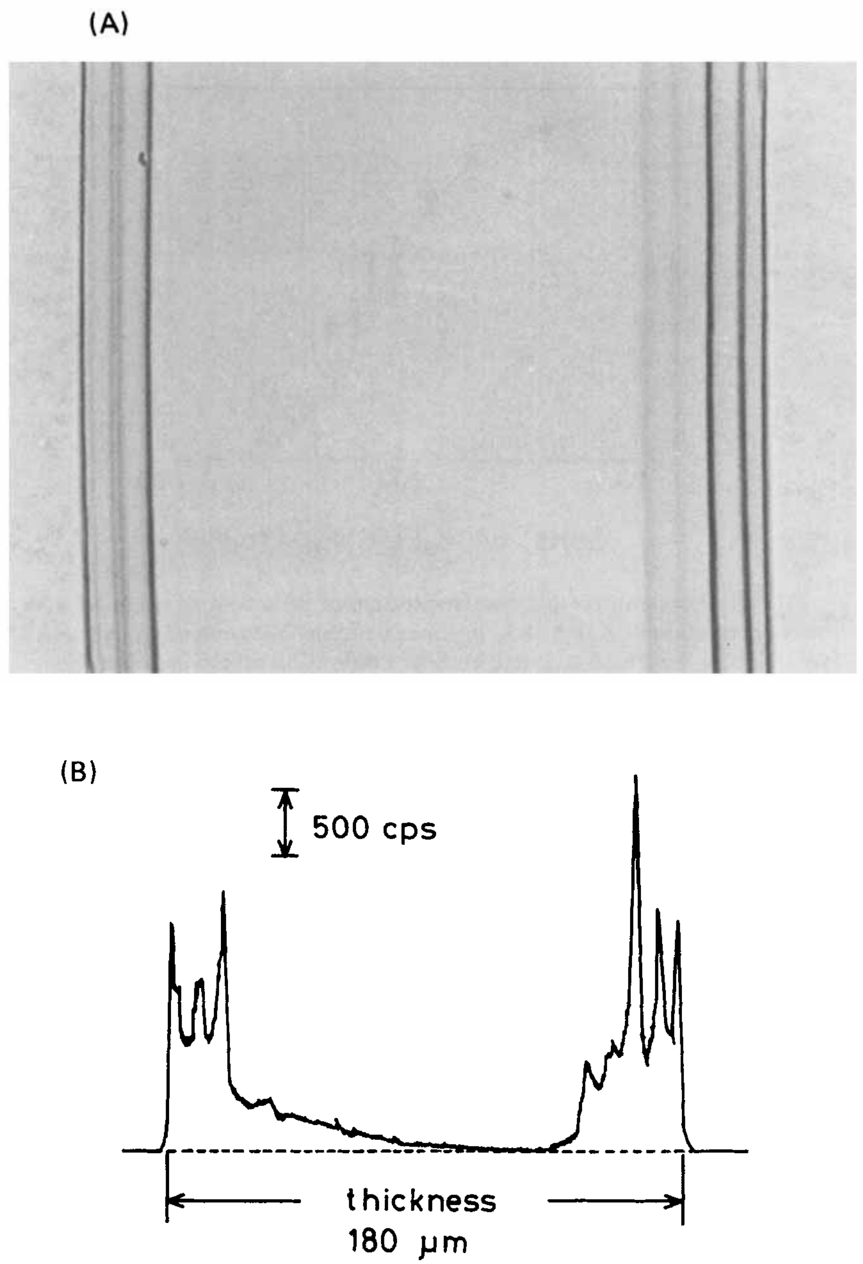

FIG. 5. Periodic pattern of PB precipitation in Nf. (A) Optical micrograph of cross section of the PB/Nf composite membrane. (B) Iron-distribution profile across the membrane.

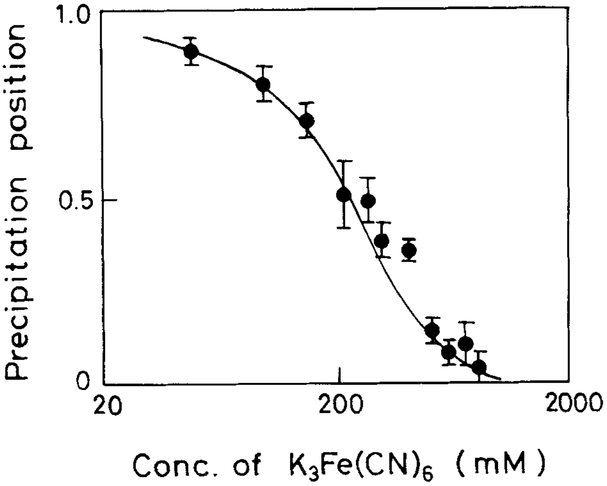

FIG. 6. Correlation of the relative position of PB precipitation in Nf with the concentration of $K_3Fe(CN)_6$ in countercurrent diffusion. The concentration of $FeCl_2$ was fixed at 2 m*M*, and the PB position on the ordinate was normalized to the thickness of Nf matrix membrane.

to deposit PB inside Nf. Otherwise, PB precipitated either in the Fe^{2+}-containing solution or in the $Fe(CN)_6{}^{3-}$-containing solution. Figure 6 demonstrates the relative position of the PB layer in Nf as a function of $K_3Fe(CN)_6$ concentration at a constant concentration of $FeCl_2$ (2 m*M*). At a lower concentration ratio of $Fe(CN)_6{}^{3-}$ to Fe^{2+}, for example, $[Fe(CN)_6{}^{3-}]/[Fe^{2+}]$ = 10-20, PB precipitated in the outermost region of the Nf facing the $K_3Fe(CN)_6$ solution. The PB layer moves toward the $FeCl_2$ solution site with increasing ratio. This could be understood as due to the significant difference in the diffusion rates of Fe^{2+} and $Fe(CN)_6{}^{3-}$ in Nf.

4. CONCLUSIONS

It was possible to regulate the position of PB precipitation in solid Nf by controlling the concentrations and directions of diffusion of Fe^{2+} and $Fe(CN)_6{}^{3-}$. In other words, various membrane structures of a PB/Nf composite could be achieved on the basis of diffusion rates of the two component ions of PB. The Fe^{2+} cation can diffuse in Nf 100 times more quickly than the $Fe(CN)_6{}^{3-}$ anion because of the electrostatic repulsion between $Fe(CN)_6{}^{3-}$ and sulfonate groups of Nf as well as the steric effect, so that Fe^{2+} can reach the surface of Nf before $Fe(CN)_6{}^{3-}$ enters the membrane when Fe^{2+} is in the Nf and $Fe(CN)_6{}^{3-}$ in the solution. On the other hand, Fe^{2+} easily gets into Nf before $Fe(CN)_6{}^{3-}$ diffuses toward the Nf surface when Fe^{2+} is in the solution and $Fe(CN)_6{}^{3-}$ is in the Nf, and PB precipitates inside Nf. Periodic patterns in the PB precipitation in Nf could not be so simply explained, but some theories are proposed for such a dissipative phenomenon [15-17], and it is important to have a complete explanation for such a physicochemical phenomenon in solid-state chemistry.

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