

## Structural Control of the Prussian Blue-Nafion Composite Membrane

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On the complex formation of Prussian Blue (PB) in a solid matrix of Nafion membrane (Nf), it was possible to control a structure of the PB-Nf composite membrane by regulating the rate and direction of diffusion in the solid phase of two component ions,  $Fe^{2+}$  and  $Fe(CN)_6^{3-}$ .

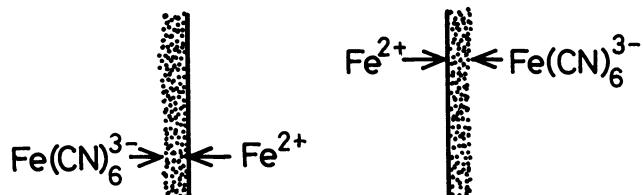
The present authors have been studying the thin-film preparation of poly-nuclear transition metal complexes on solid polymer electrolyte membranes and applications to solid-state electrochemical devices.<sup>1)</sup> Polynuclear metal complexes studied in our previous works were Prussian Blue with its analogous crosslinked complexes and Magnus Green Salt with its analogous linear-chain complexes. These kinds of compounds were difficult to be processed as a thin film or fine particle due to the least solubility and poor processabilities. Our method, which we call "Surface Complexation", has clearly solved this problem. Some interesting aspects concerning composite membrane structures have been obtained on the solid-state polymerization of transition metal complexes.<sup>2)</sup> In this paper, a correlation of the membrane structures to reaction conditions on the PB formation in Nf will be described.

PB is, as is well known, formed in solution by mixing  $Fe^{2+}$  and  $Fe(CN)_6^{3-}$  in an equimolar ratio. When this reaction was carried out in a solid phase of Nf, PB was obtained as a thin film on Nf as previously reported.<sup>1)</sup> Especially, PB was deposited preferably on the surface of Nf when Nf was immersed in  $FeCl_2$  aqueous solution and then in  $K_3Fe(CN)_6$  aqueous solution, successively, as shown in Fig. 1-A. On the other hand, if Nf was immersed in  $K_3Fe(CN)_6$  solution and then in  $FeCl_2$  solution in an opposite sequence, PB precipitated inside the matrix ( see Fig. 1-B ). It is, in general, considered that a relatively large anion like  $Fe(CN)_6^{3-}$  is hardly taken up by a polymer having anionic charges due to the electrostatic repulsion. It has, however, been recognized that even such a large anion could get into an anionic matrix with a cation accompanied as a counter ion. It was also found in the latter case that a membrane structure of the PB-Nf composite varied as a function of a concentration of the two component ions. As shown in Fig. 2-A, PB precipitated homogeneously in a whole region of the matrix at higher concentrations of  $FeCl_2$  ( $>4$  M) independent of the concentration of  $K_3Fe(CN)_6$ . PB was generally splitted into two layers below this concentration of  $FeCl_2$  ( see Fig. 2-C ). In the region B of this figure

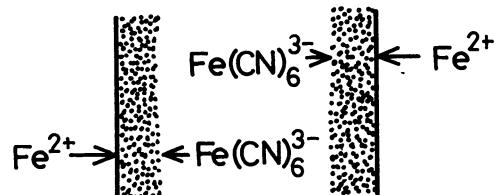
did the composite membrane vary in structure from homogeneous to splitted one depending on such uncertain factors as mixing of solution and/or membrane shape and thickness. Interestingly, PB was splitted into 7-8 narrower lines with such a periodic pattern as indicated in Fig. 2-D and Fig. 3 when the concentrations of  $\text{Fe}^{2+}$  and  $\text{Fe}(\text{CN})_6^{3-}$  were set in the region of Fig. 2-D. Figure 3 shows an optical micrograph of a cross-section of the periodic membrane with an iron distribution profile across the membrane. Each line of Fig. 3-A is in good accordance with each peak of Fig. 3-B concerning the position and density of the depositories so that the depositories in a periodic pattern in Nf could be assigned to PB itself. On determination of the membrane structures of PB-Nf composite as shown in Fig. 2, a tremendous number of samples which were obtained at various combinations of  $\text{FeCl}_2$  and  $\text{K}_3\text{Fe}(\text{CN})_6$  concentrations were examined by optical microscopy. It was especially difficult to determine the specific region for the periodic deposition like Fig. 2-D, because this phenomenon was sensitive to the reaction conditions. And also the number of lines and the line-to-line distance in Fig. 3 were changeable depending on some unknown factors involved in the reaction conditions. In any way, the results of Fig. 2 could be understood in a qualitative sense and are believed to be reproducible.

Appearance of the various membrane structures as described in Fig. 1 can be explained as follows on the basis of diffusion kinetics of component species in the solid matrix. Diffusion rates of  $\text{Fe}^{2+}$  and  $\text{Fe}(\text{CN})_6^{3-}$  in Nf were determined in our experiments to be  $10^{-6}$  and  $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ , respectively. That is,  $\text{Fe}^{2+}$  can move more quickly in Nf than does  $\text{Fe}(\text{CN})_6^{3-}$  by a factor of 100. If  $\text{Fe}^{2+}$  were in a solid phase of Nf and  $\text{Fe}(\text{CN})_6^{3-}$  in a solution,  $\text{Fe}^{2+}$  could diffuse quickly in Nf toward a solution phase before  $\text{Fe}(\text{CN})_6^{3-}$  enters the Nf membrane because of a difference in the diffusion rates in Nf and the electrostatic repulsion between  $\text{Fe}(\text{CN})_6^{3-}$  and

### (A) Stepwise method (I)



### (B) Stepwise method (II)



### (C) Counter-current method

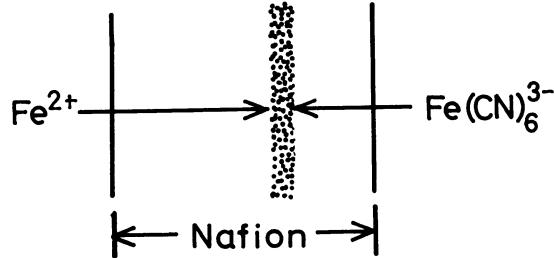


Fig. 1. Schematic representation of the procedures and precipitation patterns of PB formation in Nf.

sulfonate groups of Nf. In consequence, the two component ions could encounter with each other at the interface of Nf and solution so that PB could be deposited on the surface of Nf. On the other hand, if  $\text{Fe}(\text{CN})_6^{3-}$  were in Nf and  $\text{Fe}^{2+}$  in a solution,  $\text{Fe}^{2+}$  could enter the solid membrane before  $\text{Fe}(\text{CN})_6^{3-}$  diffuses in Nf so that PB could precipitate in the matrix in this case.

When both of the two component ions were incorporated into Nf at the same time from an opposite surface of Nf, PB precipitated in Nf to make a broader line as shown in Fig. 1-C. The precipitation position changed with the

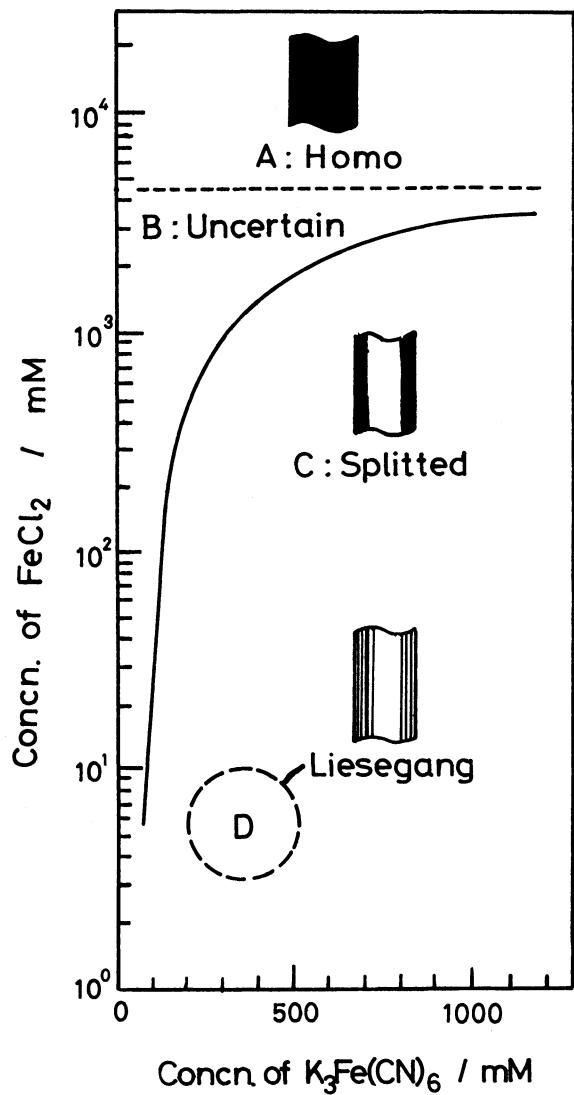


Fig. 2. Variation of membrane structures of the PB-Nf composite according to the stepwise method (III) as described in Fig. 1-B.

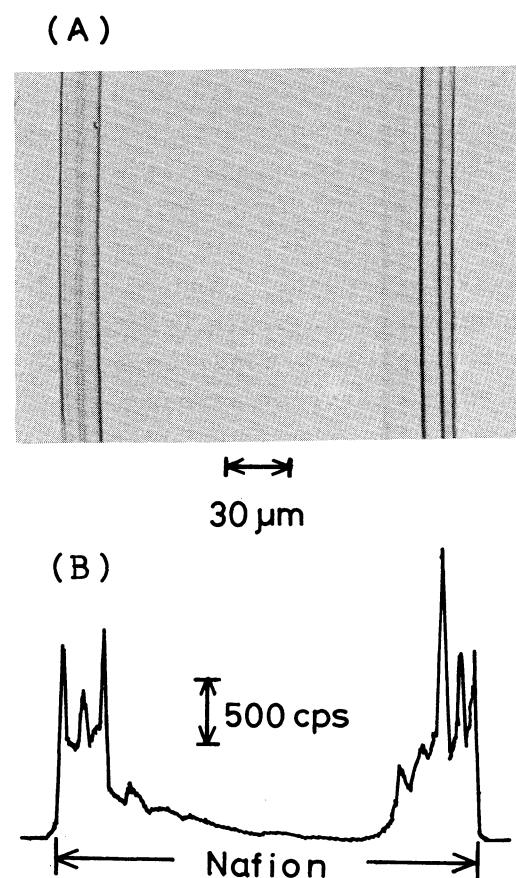


Fig. 3. Periodic pattern of PB precipitation in Nf. (A) Cross-section of the PB-Nf composite membrane, (B) Iron distribution profile across the membrane analysed by electron probe microanalysis using  $\text{Fe}(\text{K}\alpha)$  line.

concentrations of  $\text{Fe}^{2+}$  and  $\text{Fe}(\text{CN})_6^{3-}$  and approximately coincided with the calculation which is derived from Eq. 1;

$$R_{\text{PB}} = \frac{P(+)\cdot C(+)}{P(+)\cdot C(+) + P(-)\cdot C(-)} \quad (1)$$

where  $R_{\text{PB}}$  denotes a relative position of PB precipitation in Nf which was normalized by the thickness of Nf,  $P(+)$  and  $P(-)$  a diffusion rate in Nf of  $\text{Fe}^{2+}$  and  $\text{Fe}(\text{CN})_6^{3-}$ ,  $C(+)$  and  $C(-)$  a concentration of  $\text{Fe}^{2+}$  and  $\text{Fe}(\text{CN})_6^{3-}$ , respectively.

The authors have already reported the utilization of the surface-attaching type of PB-Nf membrane for an electrochemical solid cell such as a rechargeable battery and an electrochromic display device.<sup>1)</sup> The PB-impregnating Nf membrane demonstrated in this paper is also considered to be useful for other functional materials. A similar periodic interfacial phenomenon in solid polymer films as described in Fig. 2-D has been reported on the precipitation of silver halides in polyvinylalcohol<sup>3)</sup> and Nafion<sup>4)</sup> films. A number of studies have been conducted on solid-state reactions of two ionic species to yield an insoluble product under such conditions that either one or both of the reactants are supplied by diffusion across a gel. The periodic multilayers have often been observed in those systems which are called as "Liesegang phenomenon."<sup>5)</sup> Studies in dense polymer films have been less extensive than in gels and more appropriate to consider applications for fabricating new kinds of thin-layer materials which might be useful for a light modulator because of the birefringence in polarized light.

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