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# Transient Spectroscopy of the Redox Reactions of the Prussian Blue Membrane Having Electronic State Gradient

Naoki TOSHIMA,* Ru-Jang LIN, and Masao KANEKO+
Department of Industrial Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113
+The Institute of Physical and Chemical Research (Riken),
Hirosawa, Wako, Saitama 351-01

The transient spectroscopic studies were carried out on a Prussian Blue (PB) membrane coated on an ITO electrode (5 cm x 1 cm), on which an electronic state gradient was realized. An isosbestic point was clearly observed in the trasient spectral changes when the PB was oxidized upon application of a potential from open-circuit to 1.5 V difference between the membrane terminals. The transient spectra observed on stepping back to open circuit showed three isosbestic points from the entirely oxidized state to the reduced states, to which a new electron transfer process is proposed.

There is a considerable current interest in the electrochemistry of Prussian Blue (PB, unit composition: $Fe^{3+}{}_4[Fe^{II}(CN)_6]^{4-}{}_3$) from the viewpoint of the mechanism of the electron transfer and the application to a device for electrochromic display reported by Itaya, Neff et al.[1-4] and to a secondary battery.[5] Because of its high molecular weight (ca. 7.5 million),[6] it can form a membrane on various substrates. The absorption spectra of the PB membrane coated on an electrode were investigated depending on applied potentials under static conditions.[2-4] However, transient absorption spectra have not been studied. In the static absorption spectra measured under an applied potential, isosbestic points has not been observed among the different redox states, which was explained by the non-applicability of the Beer's law to the PB membrane.[4]

Recently, we have reported that, when a voltage difference of 1.5 V controlled by a potentiostat is applied between the two terminals of a PB membrane (4-5 cm in length), a sequential electronic state gradient appears on the PB membrane, where the iron complex has a sequential valence state from BB (Berlin Brown, originally named Berlin Green, a completely oxidized form of PB) at the anode terminal via PB at the center to PW (Prussian White, a completely reduced form of PB) at the cathode terminal. A color gradient is also observed along the electronic state gradient in the present planar system. This kind of gradient of the electronic state as well as the color is maintained under dynamic conditions, during which electron exchange reactions occur between the different species.[7] In order to clarify the dynamics of the electron transfer reactions in the PB membrane, we have studied the location-dependent visible spectra along the electronic state gradient on the PB membrane as well as their transient spectral changes at a fixed position of the PB membrane by using a multichannel photodiode array equipment. These studies brought about a new observation of the isosbestic points in the spectral change of the gradated PB membrane in the planar system and led to proposing a mechanism on the PB-BB (Fe(III/II)-Fe(III/III)) redox reaction.

The PB membrane was prepared by electrodeposition on a rectangular ITO electrode (5 cm x 1 cm) which was equiped with a copper lead wire at each end as previously described.$^{7)}$ In order to measure the transient spectral change and characterize the intermediates produced during the electrochemical processes, a rapid scanning multichannel photodiode array spectrometer (Otsuka Electronics Co., MCPD-110A) was used with a Leitz microscope (ERGOLUX) and a Toho Technical Research model 2000 potentiostat/galvanostat. The MCPD coupled with the Toho's model FG-02 function generator was triggered and operated by a NEC model 9801-VX personal computer.

The transient visible absorption spectra of the PB membrane in the planar system were studied in situ in a 0.5 M aqueous solution of $KNO_3$. The spectra were recorded in the range of the wavelength from 450 nm to 750 nm with a 0.4 s interval. The spectral changes with time at various positions of the PB membrane were measured while stepping the potential between the two terminals of the ITO electrode from open-circuit to 1.5 V. After keeping the potential difference of 1.5 V for a moment to ensure the sequential color gradient on the PB membrane, the potential was stepped back to open-circuit and the spectral change of the membrane was measured again. Before each experiment of the potential step cycles, the membrane was set in the 0.5 M aqueous solution of $KNO_3$ for a moment in order to recover the initial homogeneous PB state.

The transient spectral changes induced by applying the potential of 1.5 V and by stepping back the potential to open-circuit were measured at the cathode terminal, and shown in Figs. 1a and 1b, respectively. Figure 1a indicates that PB is completely reduced to PW at the cathode terminal on stepping the potential from open-circuit to 1.5 V. The wavelength at the maximum absorption (700 nm) is shifted toward longer wavelength with the increase in the degree of the reduction

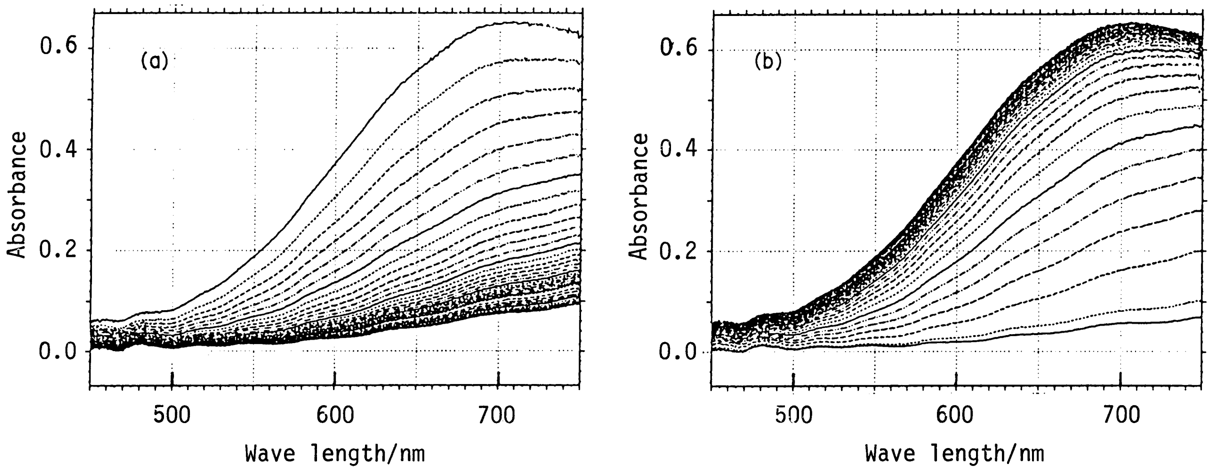


Fig. 1. Absorption spectral change of a PB membrane at the cathode terminal: (a) the reduction of PB to PW when 1.5 V is applied. (b) the oxidation of PW to PB when the potential is stepped back to open-circuit.

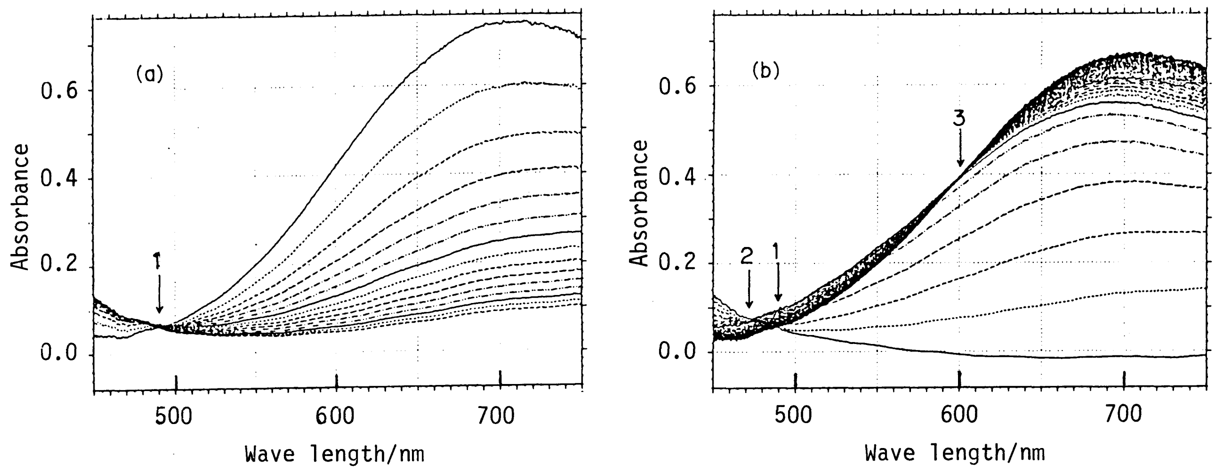


Fig. 2. Absorption spectral change of the PB membrane at the anode terminal: (a) the oxidation of PB to BB when 1.5 V is applied. (b) the reduction of BB to PB when the potential is stepped back to open-circuit.

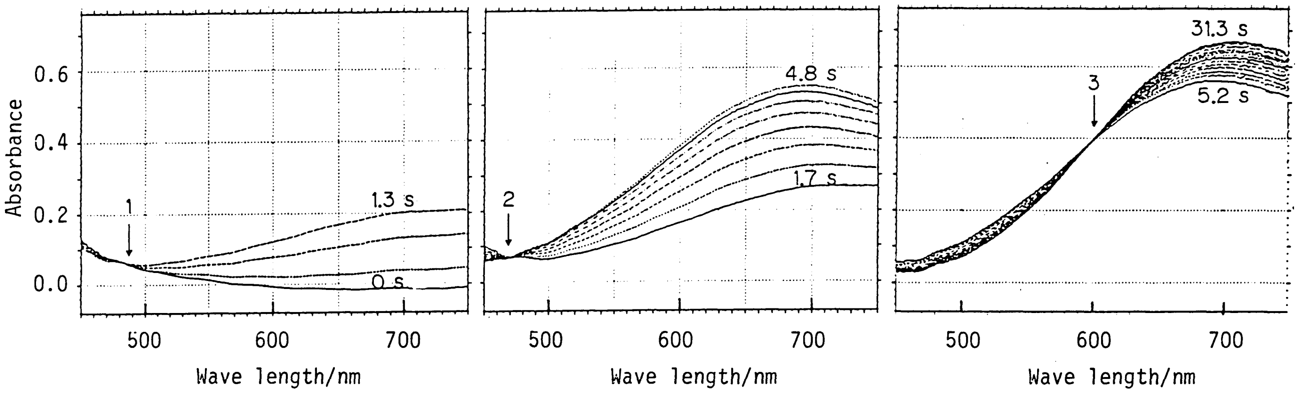
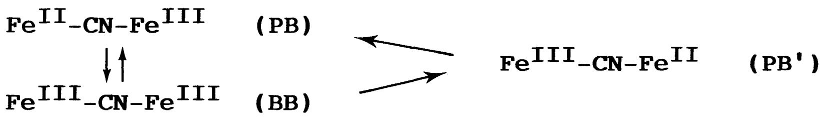


Fig. 3. Time resolved spectral changes obtained from Fig. 2 for the reduction of BB to PB.

occurring with time. Figure 1b indicates the reverse reaction from PW to PB on stepping the potential back to open-circuit.

Figures 2a and 2b show the spectral change with time at the anode terminal, where PB changes to BB when the potential of 1.5 V is applied, and the reverse reaction occurs when stepping the applied potential back to open-circuit. While there has been no report on the isosbestic point in the spectral change of a PB membrane, a clear isosbestic point is observed in the oxidation of PB to BB in Fig. 2a. Recently, Lundgren and Murray reported the presence of isosbestic points in the spectral change of a PB membrane, which were observed by very slow scanning of the potential in a three-electrode system.[8] In the present planar system, however, during the reduction of BB to PB, three isosbestic points appears with time, i.e. 485 nm at the initial stage of the reduction, 470 nm during the intermediate, and then 600 nm at the final stage, as shown in Fig. 3.[9] The spectral changes with time are reproducible both during repeated measurements and in the independent experiments. The presence of these isosbestic points, i.e. one in the oxidation of PB, and three in the reverse reaction, implies that the oxidation (PB → BB) involves only two species and that the reduction (BB → PB) is composed of three processes.

On the basis of the present observations on the isosbestic points, the following processes might be reasonably proposed for the redox reactions of PB as Scheme 1 shows: The oxidation of PB is the change from PB ($Fe^{II}$-CN-$Fe^{III}$) to BB ($Fe^{III}$-CN-$Fe^{III}$). However, the reduction of BB is not so simple as the oxidation of PB. The presence of two valence isomers, $Fe^{II}$-CN-$Fe^{III}$ (abbreviated as PB) and $Fe^{III}$-CN-$Fe^{II}$ (abbreviated as PB'), may be proposed as a possible explanation. Since PB' is unstable,[10] it should turn to PB on standing. This is consistent to the Shriver's report on the analogous compounds.[11] At the initial step of the reduction, some of the BB is directly reduced to PB producing the isosbestic point at 485 nm; this is supported by the same isosbestic point as observed in the oxidation of PB to BB. The remaining BB which is not reduced at the initial step might be reduced not to PB directly but to PB' forming the isosbestic point at 470 nm, and then PB' might turn to PB in the final stage by the valence isomerization exhibiting the isosbestic point at 600 nm. The observation of only a very small electrical charges passed during the last stage of the spectral change could support the valence isomerization from PB' to PB.



Scheme 1.

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