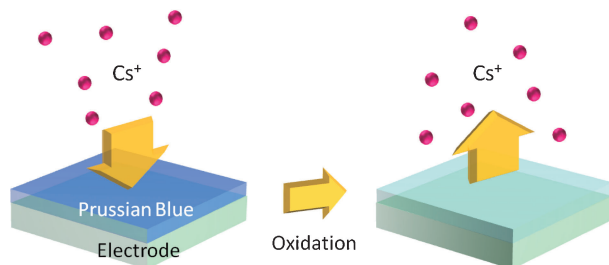# Uptake and Electrochemical Ejection of Cesium Ion by a Prussian Blue-modified Electrode

Tetsu Tatsuma,* Yoshinori Kuroiwa, Kazuyuki Ishii, Kazuaki Kudo, and Akiyoshi Sakoda
Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505

(E-mail: tatsuma@iis.u-tokyo.ac.jp)

Electrochemically deposited Prussian blue was loaded with cesium ion in a diluted aqueous CsCl solution followed by reduction or oxidation. Although reduction of Prussian blue does not increase the capacity of cesium uptake, oxidation of Prussian blue results in release of entrapped cesium ion.

REPRINTED FROM

Chemistry Letters
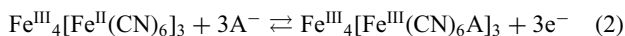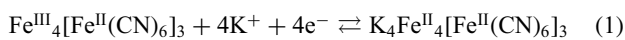
The Chemical Society of Japan

CL-140338

Uptake and Electrochemical Ejection of Cesium Ion by a Prussian Blue-modified Electrode

Tetsu Tatsuma,* Yoshinori Kuroiwa, Kazuyuki Ishii, Kazuaki Kudo, and Akiyoshi Sakoda
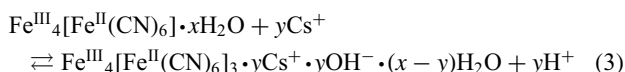*Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba, Meguro-ku, Tokyo 153-8505*

(E-mail: tatsuma@iis.u-tokyo.ac.jp)

Prussian blue ($Fe^{III}_4[Fe^{II}(CN)_6]_3$) electrochemically deposited on an indium tin oxide electrode was loaded with cesium ion in a diluted aqueous CsCl solution (ca. 40 ppb) followed by reduction or oxidation. Although reduction of Prussian blue does not increase the capacity of cesium uptake, oxidation of Prussian blue releases the entrapped cesium ion.

Prussian blue ($Fe^{III}_4[Fe^{II}(CN)_6]_3$, PB)[1] has been practically used as a sorbent for radioactive Cs^+ ($^{134}Cs^+$ and $^{137}Cs^+$) released to the environment in the atomic weapon tests in the 1960s and the Chernobyl nuclear plant accident in 1986.[2–4] It is, therefore, expected to be effective for the decontamination of the fallout due to the Fukushima nuclear accident in 2011.[5–7] PB has also been known and used as an electrochromic material, because its color depends on the redox state.[8–11] Its blue color is bleached to colorless by reduction to Prussian white (PW, or Everitt's salt) (eq 1) and is changed to pale yellow or green by oxidation to Prussian yellow (PY, or Berlin green) in the presence of K^+ (eq 2).[11]

$$Fe^{III}_4[Fe^{II}(CN)_6]_3 + 4K^+ + 4e^- \rightleftarrows K_4Fe^{II}_4[Fe^{II}(CN)_6]_3 \quad (1)$$

$$Fe^{III}_4[Fe^{II}(CN)_6]_3 + 3A^- \rightleftarrows Fe^{III}_4[Fe^{III}(CN)_6A]_3 + 3e^- \quad (2)$$

where A^- is an anion in the solution. Reduction[10,12] and oxidation[12] of PB are also possible in the presence of Cs^+. On the basis of an analogy from those equations, one may expect that reduction of PB will improve the Cs^+-sorption capacity and that oxidation of PB will result in the uptake of A^-. However, neutral PB containing water molecules is known to absorb Cs^+ before reduction[13,14] because of an exchange with H^+ (eq 3).[15]

$$Fe^{III}_4[Fe^{II}(CN)_6] \cdot xH_2O + yCs^+$$
$$\rightleftarrows Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot yCs^+ \cdot yOH^- \cdot (x-y)H_2O + yH^+ \quad (3)$$

Therefore, the above-mentioned expectation might not hold for the Cs^+-containing PB. Nevertheless, precise ion-exchange behavior of the Cs^+-containing PB upon its reduction and oxidation has not yet been studied to the best of our knowledge, particularly at low Cs^+ concentrations. In the case of nickel(II)[16,17] and copper(II)[18,19] hexacyanoferrate(II), it is reported that absorbed Cs^+ is released upon oxidation to hexacyanoferrate(III). Similar release of Cs^+ may be expected for the oxidation of PB to PY, as well as for the release of H^+ and $Fe^{2+/3+}$ and uptake of OH^- and other coexisting anions. In the present work, we prepared a PB film on a transparent indium tin oxide (ITO) electrode and loaded it with Cs^+ at ca. 40 ppm. Then, we polarized the electrode to reduce or oxidize the film and examined the retention of the preabsorbed Cs^+. As a result, we found that Cs^+ is retained in the film when it is reduced and that Cs^+ is released when the film is oxidized.

PB was electrodeposited onto a clean ITO-coated glass plate (Kinoene Kogaku) (electrode area: 2 cm²) from an aqueous solution containing 0.02 M $FeCl_3$, 0.02 M $K_3[Fe(CN)_6]$, and

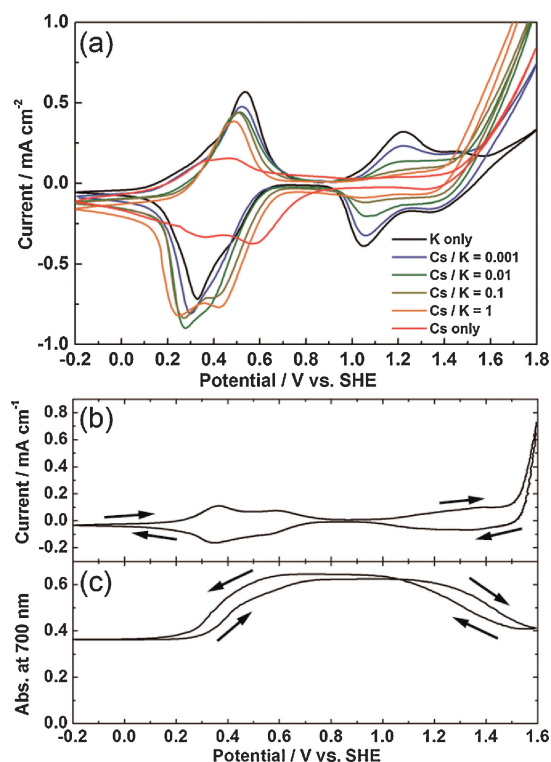**Figure 1.** (a) Cyclic voltammograms of the PB film in 0.01 M HCl solution containing KCl and CsCl ([KCl] + [CsCl] = 1.0 M) at 50 mV s⁻¹ and (b) that in 0.01 M CsCl at 10 mV s⁻¹ with (c) absorbance changes at 700 nm.

0.01 M HCl at a constant cathodic current of 20 μA cm⁻² for 240 s.[9,10] The as-deposited blue film exhibits a broad absorption peak at ca. 700 nm, which is ascribed to charge transfer between $[Fe^{II}(CN)_6]^{4-}$ and Fe^{III}.[20] The average thickness of the film observed by scanning electron microscopy is ca. 100 nm, which corresponds to ca. 30 nmol of PB deposited on the electrode. The deposited PB was dissolved in 0.1 M aqueous ammonia, and the amount of Fe in the solution was determined by inductively coupled plasma mass spectrometry (ICP-MS, by using SPQ-9000, SII) to be 210 nmol, which corresponds to 30 nmol of PB. The Coulomb efficiency of the electrodeposition was ca. 90%.

The PB-coated electrode was characterized by cyclic voltammetry at 50 mV s⁻¹ in a 0.01 M aqueous HCl solution containing 1 M KCl by using a Pt counter electrode and a Ag|AgCl reference electrode (Figure 1a, black curve). The initial open circuit potential was ca. +0.5 V vs. standard hydrogen electrode (SHE). It is obvious that the PB film is reduced at ca. +0.4 V and oxidized at ca. +1.2 V. These redox reactions were repeatable. After the electrode was poised at +0.1 V for 2 min, the blue color was almost bleached; PB was

reduced to PW. On the other hand, the color was changed to pale green after polarization at $+1.6$ V for 2 min; PB was oxidized to PY. Thus, the electrochemical behavior of PB was essentially the same as that reported previously.[9–12]

The electrochemistry of PB was also examined in a 0.01 M aqueous HCl solution containing KCl and/or CsCl (Figure 1a). The total concentration of K^+ and Cs^+ was 1.0 M. In our experiments, we used nonradiative Cs^+ because its size is essentially the same as those of radioactive $^{134}Cs^+$ and $^{137}Cs^+$.

The redox peaks were suppressed as the Cs^+ content increased, in particular for the PB/PY redox reactions, as reported previously.[12] However, the absorbance at 700 nm decreased obviously in a cyclic voltammetry in 0.01 M CsCl, at more negative potentials than $+0.7$ V and more positive potentials than $+0.9$ V (Figures 1b and 1c). These redox reactions were repeatable with reversible absorbance changes. We, therefore, conclude that the PB film can be reduced and oxidized, at least in part, even in the presence of Cs^+. In addition, the anodic current at more positive potentials than $+1.3$ V was enhanced in the presence of Cs^+ at the PB-coated electrode, whereas no obvious current was observed at a bare ITO electrode. The charges passed in this potential region in one cycle ($6–9$ mC cm^{-2}) are larger than that required for the PB film deposition (4.8 mC cm^{-2}). Therefore, the current might reflect that the PB film has higher electrocatalytic activity for the oxidation of water and/or Cl$^-$, particularly in the presence of Cs^+.

The distribution coefficient K_d for the Cs^+ sorption into the PB film was also examined. An as-prepared PB film was soaked in a CsCl solution ($1–100$ ppb, 20 mL, pH 5.5, ca. 20 °C) for at least 15 h, and the amount of Cs^+ left in the solution was determined by ICP-MS. The distribution coefficient K_d was evaluated from the relationship between the amount of Cs^+ in the film and the Cs^+ concentration in the solution at equilibrium to be 8.7×10^5 mL g^{-1}. This value is in the range of the reported values ($3 \times 10^5–3 \times 10^6$ mL g^{-1}).[21–23]

Next, the retention of Cs^+ was examined after the reduction and oxidation of PB. An as-prepared electrode with the PB coating was soaked in a 100-ppb CsCl solution (20 mL; 15.0 nmol of Cs^+ is contained) for at least 12 h. A 2-mL aliquot of the solution was sampled, and the amount of Cs^+ absorbed by PB was determined by ICP-MS to be 9.05 ± 0.8 nmol (average $\pm$ standard deviation, $n = 12$). Then, the electrode was polarized at a certain potential (varying from $+0.4$ to $+1.3$ V) for 1 h to reduce or oxidize the PB film. The Cs^+ concentration of the solution was measured again, so that %retention of Cs^+ in the film was determined and plotted as a function of the electrode potential in Figure 2.

When the PB film is completely reduced to PW, ca. 120 nmol of electrons must be injected into the film. At $+0.4$ V, 20 ± 1 nmol ($n = 3$) of electrons was consumed for the reduction, suggesting that $\leq 17\%$ of the PB film was reduced. Injection of ca. 20 nmol electrons into the film must be accompanied by the injection of the same amount of cations or ejection of anions to maintain charge neutrality. In a solution of a potassium salt, K^+ is injected into the film (eq 1).[11] In the present case, however, no further uptake of Cs^+ was observed. This might suggest that the negative charges generated in the reduced film is compensated by H^+ uptake or OH$^-$ release, which gives rise to only a slight pH shift of <0.2 in the solution.
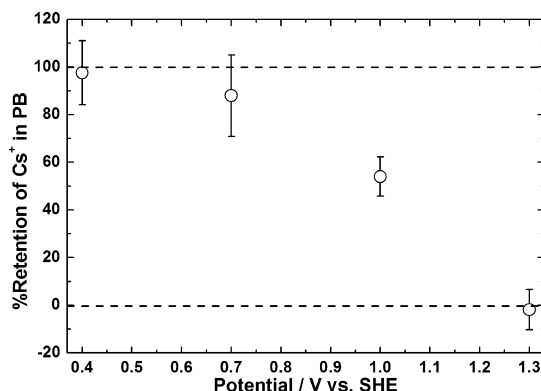

Figure 2. Amount of Cs^+ retained in the PB film after potential application of 1 h.

On the other hand, ca. 90 nmol of electrons must be removed from the film for total oxidation of the PB film to PY. It should be accompanied by ejection of the same amount of cations or injection of anions. In our experiment at $+1.3$ V, 96 ± 4 nmol ($n = 3$) of electrons was taken out of the film, and the film ejected most of the preloaded Cs^+ (ca. 9 nmol). Because PY may catalyze the oxidation of water or Cl$^-$ as mentioned above, >93 nmol of electrons might be consumed for the catalytic oxidation. The oxidation resulted in the loss of ca. 20% PB, which might be responsible for the Cs^+ release in part, possibly due to mechanical stress generated by the ejection of bulky Cs^+.

In conclusion, reduction of Cs^+-containing PB does not cause further uptake of Cs^+, whereas oxidation results in the release of Cs^+. When PB is used as a sorbent for radioactive Cs^+, extensive oxidation of PB should be avoided not to deteriorate the sorption ability and to prevent the film from unintended release of Cs^+.

References
1 J. F. Keggin, F. D. Miles, *Nature* **1936**, *137*, 577.
2 V. Nigrović, *Int. J. Radiat. Biol.* **1963**, *7*, 307.
3 G. Voigt, *Sci. Total Environ.* **1993**, *137*, 205.
4 J. Pearce, *Food Chem. Toxicol.* **1994**, *32*, 577.
5 A. Kitajima, H. Tanaka, N. Minami, K. Yoshino, T. Kawamoto, *Chem. Lett.* **2012**, *41*, 1473.
6 T. Sasaki, S. Tanaka, *Chem. Lett.* **2012**, *41*, 32.
7 K. Ishii, M. Obi, K. Kudo, K. Akagawa, T. Tatsuma, A. Sakoda, PCT Int. Appl. WO2013027652-A1, **2012**.
8 V. D. Neff, *J. Electrochem. Soc.* **1978**, *125*, 886.
9 K. Itaya, K. Shibayama, H. Akahoshi, S. Toshima, *J. Appl. Phys.* **1982**, *53*, 804.
10 K. Itaya, T. Ataka, S. Toshima, *J. Am. Chem. Soc.* **1982**, *104*, 4767.
11 K. Itaya, I. Uchida, V. D. Neff, *Acc. Chem. Res.* **1986**, *19*, 162.
12 J. J. García-Jareño, J. Navarro-Laboulais, A. Sanmatías, F. Vicente, *Electrochim. Acta* **1998**, *43*, 1045.
13 T. Ikeshoji, T. Iwasaki, *Inorg. Chem.* **1988**, *27*, 1123.

14 T. Ikeshoji, *J. Electrochem. Soc.* **1986**, *133*, 2108.

15 M. Ishizaki, S. Akiba, A. Ohtani, Y. Hoshi, K. Ono, M. Matsuba, T. Togashi, K. Kanaizuka, M. Sakamoto, A. Takahashi, T. Kawamoto, H. Tanaka, M. Watanabe, M. Arisaka, T. Nankawa, M. Kurihara, *Dalton Trans.* **2013**, *42*, 16049.

16 M. A. Lilga, R. J. Orth, J. P. H. Sukamto, S. M. Haight, D. T. Schwartz, *Sep. Purif. Technol.* **1997**, *11*, 147.

17 M. A. Lilga, R. J. Orth, J. P. H. Sukamto, S. D. Rassat, J. D. Genders, R. Gopal, *Sep. Purif. Technol.* **2001**, *24*, 451.

18 R. Chen, H. Tanaka, T. Kawamoto, M. Asai, C. Fukushima, M. Kurihara, M. Watanabe, M. Arisaka, T. Nankawa, *Electrochem. Commun.* **2012**, *25*, 23.

19 R. Chen, H. Tanaka, T. Kawamoto, M. Asai, C. Fukushima, H. Na, M. Kurihara, M. Watanabe, M. Arisaka, T. Nankawa, *Electrochim. Acta* **2013**, *87*, 119.

20 M. B. Robin, *Inorg. Chem.* **1962**, *1*, 337.

21 T. Sangvanich, V. Sukwarotwat, R. J. Wiacek, R. M. Grudzien, G. E. Fryxell, R. S. Addleman, C. Timchalk, W. Yantasee, *J. Hazard. Mater.* **2010**, *182*, 225.

22 C. Thammawong, P. Opaprakasit, P. Tangboriboonrat, P. Sreearunothai, *J. Nanopart. Res.* **2013**, *15*, 1689.

23 H. Yang, L. Sun, J. Zhai, H. Li, Y. Zhao, H. Yu, *J. Mater. Chem. A* **2014**, *2*, 326.