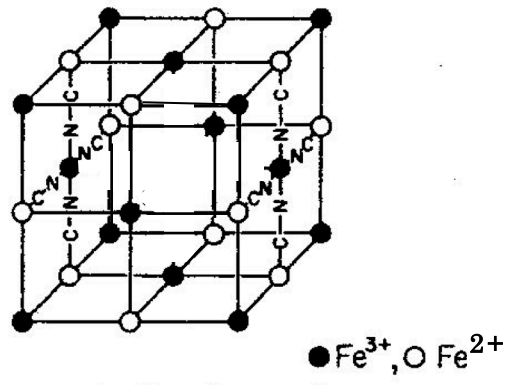
Redox reaction of metal complex.

Prussian blue (PB) is one of the famous blue pigments. It is a mixed valent metal complex, containing ferrous ion Fe^{2+} and ferric ion Fe^{3+} with a cross-linkage of cyanide ion (CN^-). PB changes its color in the oxidation state and in the reduction state. The valence state of iron ion of PB : Fe^{2+}/Fe^{3+} changes to Fe^{3+}/Fe^{3+} in the oxidation state, which is called Prussian brown (PBr) from its color. The valence state changes to Fe^{2+}/Fe^{2+} in the reduction state, which is called Prussian white (PW) from its color.



Crystal structure of PB

In this experiment,

1. We prepare the solutions of Fe^{2+} ion, Fe^{3+} ion, $[Fe^{2+}(CN)_6]^{4-}$ ion and $[Fe^{3+}(CN)_6]^{3-}$ ion. After that we mix them and observe the color of three valence states of the complexes of Fe^{2+}/Fe^{3+}(PB), Fe^{3+}/Fe^{3+} (PBr) and Fe^{2+}/Fe^{2+} (PW).

2. We observe the reduction of Fe^{3+}/Fe^{3+} (PBr) with reducing agent to Fe^{2+}/Fe^{3+}(PB) and Fe^{2+}/Fe^{2+} (PW). After that we observe oxidation of Fe^{2+}/Fe^{2+} (PW) with oxidizing agent to Fe^{2+}/Fe^{3+}(PB).

3. We observe electrochemical PB deposition onto the indium tin oxide (ITO)-coated glass supporting electrodes. This PB deposition is the electrochemically reduction of Fe^{3+}/Fe^{3+} (PBr) to Fe^{2+}/Fe^{3+}(PB) via one electron transfer.

4. We make a small rechargeable cell with two PB deposited ITO-coated electrodes. After that we observe the color change of PB with electrochemical reduction in one side and electrochemical oxidation in the other side.

Materials

Iron(III) chloride hexahydrate $FeCl_3 \cdot 6H_2O$,

Iron(II) Sulfate Heptahydrate $FeSO_4 \cdot 7H_2O$,

Potassium hexacyanoferrate(II) trihydrate $K_4Fe(CN)_6 \cdot 3H_2O$ (Potassium ferrocyanide)

Potassium hexacyanoferrate(III) $K_3Fe(CN)_6$ (Potassium ferricyanide)

Sodium sulfite Na_2SO_3, Ascorbic acid $C_6H_8O_6$

0.01 M(=mol/L) HCl aqueous solution

Procedure

Preparing solutions

1. Record the color of crystal in the bottles on Table 1. Add 30mL of 0.01M HCl solution to the bottle ① and ③(large-size bottles), respectively. Add 10mL of 0.01M HCl solution to the bottle ② and ④, respectively. Then move the bottles gentry in a circular motion and dissolve the crystals (Don't shake the bottles).

Table 1 Color of crystal and its solution

	Bottle ① $FeCl_3 \cdot 6H_2O$ (Fe^{3+})	Bottle ② $FeSO_4 \cdot 7H_2O$ (Fe^{2+})	Bottle ③ $K_3Fe(CN)_6$ (Fe^{3+})	Bottle ④ $K_4Fe(CN)_6 \cdot 3H_2O$ (Fe^{2+})
Color of crystal				
Color of solution				

Observation of the color of complex

2. Label four test tubes with the numbers of ⑤, ⑥, ⑦ and ⑧. Looking at Table 2, pour two solutions to each test tube up to the line on the tube. (Volume of each solution is about 2 mL) . Observe and record the color of each solution into Table 2.

Table 2 Observation the color of three kind of complex PBr[Fe^{3+}/Fe^{3+}], PB[Fe^{2+}/Fe^{3+}], and PW [Fe^{2+}/Fe^{2+}].

	Bottle ③ (Fe^{3+}) $K_3[Fe(CN)_6]$ solution	Bottle ④ (Fe^{2+}) $K_4[Fe(CN)_6]$ solution
Bottle ① (Fe^{3+}) $FeCl_3$ solution	test tube ⑤ [Fe^{3+}/Fe^{3+}] (①+③)	test tube ⑥ [Fe^{2+}/Fe^{3+}] (①+④)
Bottle ② (Fe^{2+}) $FeSO_4$ solution	test tube ⑦ [Fe^{2+}/Fe^{3+}] (②+③)	test tube ⑧ [Fe^{2+}/Fe^{2+}] (②+④) test tube⑧' [Fe^{2+}/Fe^{2+}]

Observation of the reduction reaction with reducing agent

3. Add a few particles of ascorbic acid to the test tube ⑤ and observe its color change. After that, add whole amount of ascorbic acid to the test tube ⑤ and dissolve them. Observe the color.

4. Add whole amount of Na_2SO_3 to the test tube ⑤ and dissolve them. Observe the color change after leaving the test tube 5 minutes. Change the label of test tube ⑤ to ⑧'. Record the color of solution ⑧' into Table 2.

Observation of the oxidation reaction with oxidizing agent

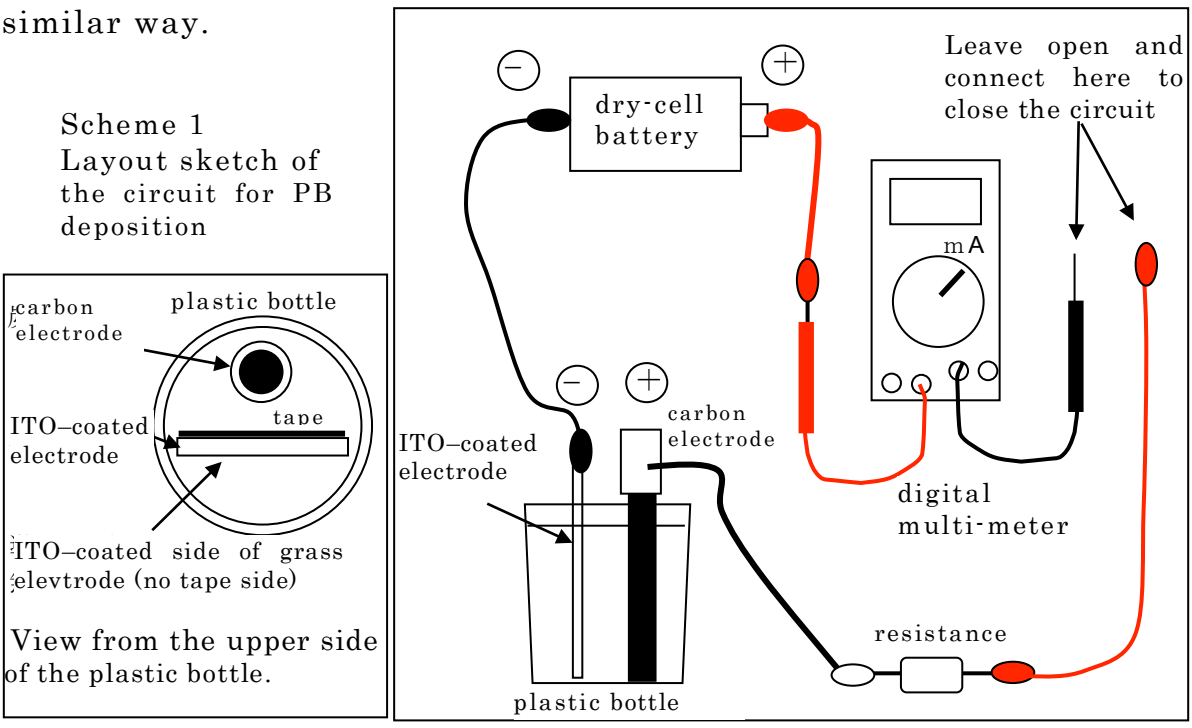
5. Pour the half of the solution ⑧' to test tube ⑨. Add H_2O_2 solution to test tube ⑨ and observe the color.

Electrochemical PB deposition onto ITO-coated glass electrodes

6. Pour the same volume of the solutions ① and ③ to a small plastic bottle (up to each line written on the bottle).

7. Immerse ITO-coated glass with red tape into the solution, and make a open circuit as written in the Scheme 1. Close the circuit for 2 minutes. Immerse PB deposited ITO-coated glass into KCl solution.
Deposit PB on the ITO-coated glass with black tape for 3 minutes in a similar way.

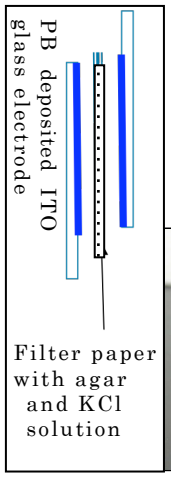
Scheme 1
Layout sketch of the circuit for PB deposition



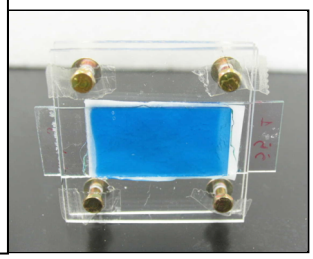
<Observation>

Observation of the electrochemical reaction on a rechargeable cell

8. Assemble a PB cell as shown in Scheme 2 by using the two PB deposited ITO-coated glass electrodes and filter paper with agar containing KCl solution.



Scheme 2
Layout sketch of PB cell



9. Connect plus side of the dry-cell battery to the PB deposited ITO-coated glass with red tape and minus side to the one with black tape directly and apply electrical current for about 1 minute. Disconnect the dry-cell battery from the PB cell. Observe the color change of the both side. Short both side of PB cell with a cable. Observe the color change of the both side. Repeat three times of charging and short circuit procedures.
<Observation>

10. After recharging PB cell, connect a musical element to the PB cell.
<Observation>

Notes

Sodium sulfite Na_2SO_3 is used as food preservatives i.e. antioxidant for wine etc.

Ascorbic acid is called Vitamin C, and works as antioxidant.