In Situ X-ray Diffraction Measurement of a Prussian Blue Modified Electrode

Sir:

Prussian blue (PB: $Fe_4[Fe(CN)_6]_3$) is one of many well-known mixed-valence compounds,[1] and a number of works on its electrochemistry have appeared following the successful preparation of a PB-modified electrode.[1-9] Cations penetrate into PB at about 0.2 V vs SCE in aqueous solutions as the iron centers are reduced from Fe^{III} to Fe^{II} and the color changes from blue to white. The reduced form is often termed Everitt white. From the different features in cyclic voltammograms measured in several kinds of supporting electrolytes,[1,2,4,7] it was shown that the cations of smaller sizes in the Stokes radii penetrate more easily.[1,4,7] This result was confirmed by a reduction–oxidation process of PB in mixed solutions of alkali-metal ions, in which selective recovery was possible in the order of $Li \ll Na < K < Rb \ll Cs$.[9] One question that occurred to us was why the ions with smaller Stokes radii could penetrate easily even though those ions are crystallographically larger. Several interpretations might be possible to answer this question. One is that the ions with smaller Stokes radii may have a smaller kinetic barrier to penetrate into the PB lattice. Another is that they may have larger thermodynamic stability in the PB lattice. In the latter case, it is expected that a small change in the lattice constant takes place during the redox reaction in PB. This paper concerns an in situ X-ray diffraction study on a PB-modified electrode that was controlled at various redox potentials. The result showed that the crystallographically larger ions increased the lattice constant more extensively.

The in situ measurement of X-ray diffraction in electrochemical studies has been shown to be a very powerful technique by several groups.[10-12] The electrochemical cell used is illustrated in Figure 1. PB was deposited from a solution of $K_3Fe(CN)_6$ (10 mM) + $FeCl_3$ (10 mM) + HCl (pH 2) with a cathodic current (20 $\mu A/cm^2$, 20 min) on gold that was sputtered onto a membrane filter (cellulose nitrate, pore size in catalog 0.1 μm). PB of ca. 2×10^{-6} mol of Fe/cm^2 was deposited on the membrane filter (ca. 4 cm^2 in an apparent area). There was a contribution other than the electrochemical deposition. The PB-coated membrane filter was covered by an X-ray-transparent polyethylene film. A counter electrode (Ag/AgCl) separated by sintered glass and glass fiber paper was placed behind the membrane. Thus, the current flowed to the PB from the backside through the membrane filter and the sintered glass. This arrangement made it possible to measure X-ray diffraction in situ from highly resistant PB with a short polarization time (ca. 20 min). An aqueous solution of 1 M LiCl, NaCl, KCl, RbCl, or CsCl with 0.0001 N HCl filled the electrochemical cell, which was mounted in an X-ray powder diffractometer (Rigaku Co., Ltd. RAD-II B) operated under the following conditions: X-ray, Cu Kα radiation monochromatized with a graphite crystal; scan speed, 2°/min in 2θ; sampling step, 0.02°; number of smoothing points, 15; scan range, 4–66° in 2θ. The redox state of PB was controlled at −0.1 to +0.4 V vs the counter electrode (Ag/AgCl) by a potentiostat to measure the X-ray diffraction from PB.

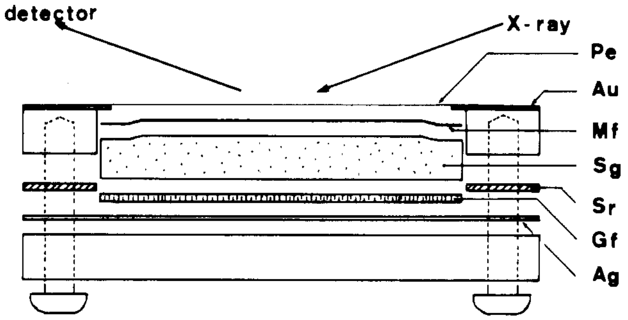

Figure 1. Electrochemical cell for in situ X-ray diffraction measurement. Pe = polyethylene film; Au = gold plate; Mf = membrane filter (Prussian blue is coated on the Pe side); Sg = sintered glass; Sr = silicon rubber; Gf = glass fiber paper; Ag = silver plate coated with AgCl.

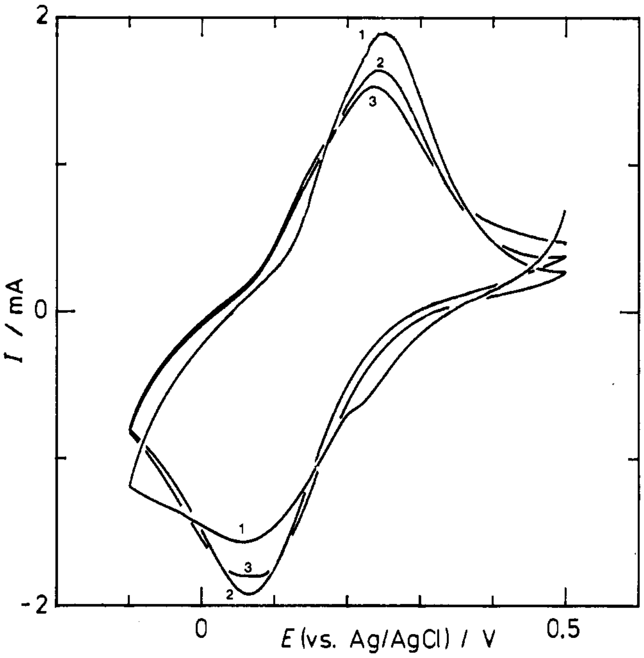

Figure 2. Typical cyclic voltammogram measured in a KCl solution with the in situ electrochemical cell (two-electrode cell) at a scan rate of 1 mV/s. (Numbers near the curves indicate those of the cycled scans.)

A typical cyclic voltammogram obtained by this cell (two-electrode arrangement) is shown in Figure 2, illustrating how well PB works as a redox electrode. Though cathodic and anodic peaks should be symmetrical, diffuse peaks due to a slow diffusion process in a large amount of PB were obtained. The peak separation decreased at lower scan rates.

The basic structure of PB is a three-dimensional polymeric network consisting of alternating ferric and ferrous ions (on cubic lattice sites) bridged by cyanide ligands; a_0 (Fe^{II}–C–N–Fe^{III}–N–C–Fe^{II} distance) = 10.1 Å.[13-15] Some typical in situ X-ray diffraction patterns from PB and its reduced forms are shown in Figure 3. The in situ X-ray diffraction patterns from the freshly prepared PB in LiCl, NaCl, and KCl solutions (see Figure 3a) were identical with those of PB already published.[13-15] However, in the solution containing Cs^+, the diffraction pattern (Figure 3c) almost identical with those of PB containing Cs^+, $CsFe[Fe(CN)_6]$ and $Cs_{13}Fe_4[Fe(CN)_6]_7$,[17] was obtained only by immersing it in that solution. In the solution containing Rb^+, a small change in the patterns was observed when it was immersed in the solution. This indicates that Cs^+ (and a small amount of Rb^+) penetrates into the PB lattice with no electroreduction.

Larger changes in the intensity of the diffraction peaks were observed following the reduction in the solutions containing al-

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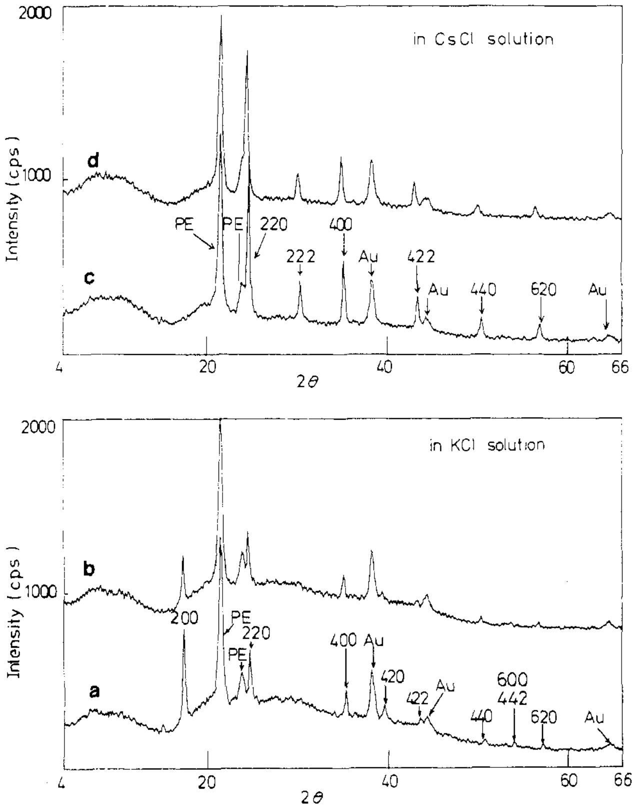

Figure 3. Typical X-ray diffraction patterns measured in situ from Prussian blue and its reduced forms prepared by electroreduction in KCl (a, b) and CsCl (c, d) solutions: (a, c) PB; (b, d) PB potentiostated at 0 V in KCl solution or −0.05 V in CsCl vs Ag/AgCl.

kali-metal ions of a larger atomic number. The diffraction intensities of the individual peaks changed as follows (as changes from a to b and from c to d in Figure 3): *hkl* of increasing peaks, 220 and 222; *hkl* of decreasing peaks, 200, 420, 442, and 600. These intensity changes show that the alkali-metal ions penetrate into the PB lattice because of the electroreduction.

It has been proposed that cations are inserted into PB after reduction without changing the lattice structure[11] or a_0.[2,16] In this measurement, no change in the cubic cell structure was observed after electroreduction. However, positions and intensities of the diffraction peaks changed with the potentials. They changed continuously with neither a peak split nor a long spacing reflection. Therefore, the cations must penetrate into the PB lattice and occupy a site randomly as though forming a solid solution. The lattice constants of the cubic cell at the various potentials are illustrated in Figure 4. They were obtained as the average values of a_0 from d spacings of four to eight diffraction peaks after correction using the 110 peak of gold ($2\theta = 38.19°$). In the case of Cs^+, a_0 was shifted with no electroreduction due to the penetration of Cs^+ as described above. During the oxidation of Everitt white, the lattice constants were changed almost reversibly, as shown by the open symbols in Figure 4. Under these experimental conditions, the separation of PB from the electrode, which has been reported in cyclic voltammetry measurements in LiCl and NaCl solutions,[4] was not observed. This may be due to using a soft electrode like cellulose instead of a conventional platinum electrode.

During the penetration of the cations, crystallographically larger cations increased a_0 more extensively. Increases in a_0 observed at −0.1 to 0 V from freshly prepared PB in the solution with no alkali-metal ion (a_0 = 10.16 Å indicated by the + symbol in Figure 4) were as follows: Li^+, 0.036 Å; Na^+, 0.094 Å; K^+, 0.082 Å; Rb^+, 0.116 Å; Cs^+, 0.152 Å (with errors of ±0.012 Å). Since the residual currents at the potentials less than 0.2 V were quite high, it was impossible to calculate precisely how many cations penetrated into a unit cell of PB. The source of the residual current was not identified completely, but it might be due to the high activity on the surface of the sputtered gold. Roughly estimated changes in the lattice constant by a charge of 1 faraday/mole of Fe in PB were 0.22 ± 0.06 Å for Na^+, K^+, Rb^+, and Cs^+ and 0.12 ± 0.04 Å for Li^+ from an a_0 vs charge plot (potential > 0.2 V) and a chemical analysis of the PB film. The ions penetrating with more difficulty into the lattice like Li^+ seemed to have a crystallographically small effect. Therefore, it is implied that there is a contribution from the kinetic effect in the easy penetration of ions with small Stokes radii.

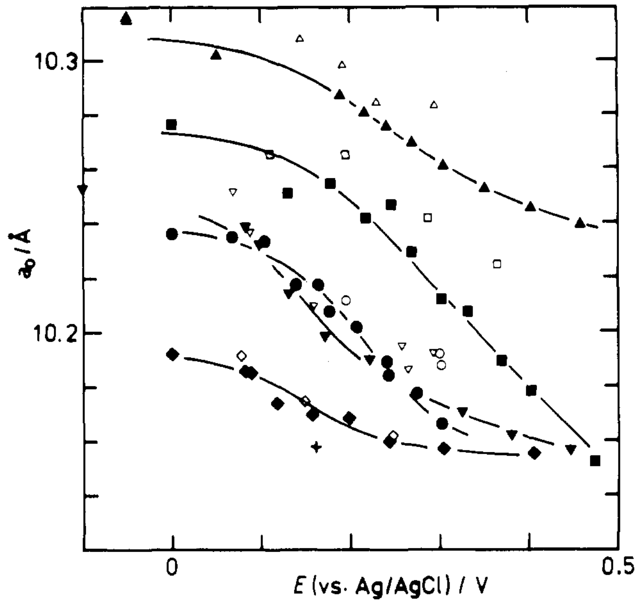

Figure 4. Lattice constant change of Prussian blue during the reduction in 1 M alkali-metal chloride solutions with 0.0001 N HCl: ▲, Cs; ■, Rb; ●, K; ▼, Na; ◆, Li; +, no alkali-metal chloride. (Open symbols show a_0 measured during the oxidation after the reduction of PB.)

In order to confirm these conclusions, it is important to measure a_0 vs charge instead of a_0 vs potential. This requires an appropriate electrochemical system that has a low residual current. Measurement of penetration of ammonium ion and tetraalkylammonium ions would also provide further evidence for the above conclusion. It is also necessary to calculate the structural parameters of PB containing alkali-metal ions to determine the penetrating position in the PB lattice. These studies are currently in progress.

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Registry No. $Fe_4[Fe(CN)_6]_3$, 14038-43-8; $[Fe(CN)_6]^{4-}$, 13408-63-4; CsCl, 7647-17-8; RbCl, 7791-11-9; KCl, 7447-40-7; NaCl, 7647-14-5; LiCl, 7447-41-8; Cs, 7440-46-2; Rb, 7440-17-7; K, 7440-09-7; Na, 7440-23-5; Li, 7439-93-2.

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NMR Studies of the Complexes *trans*-$[M(\eta^2\text{-}H_2)(H)(Ph_2PCH_2CH_2PEt_2)_2]X$ (M = Fe, X = BPh_4; M = Os, X = BF_4): Evidence for Unexpected Shortening of the H–H Bond

Sir:

Several recent papers describe how changes in coligands adjacent to the η^2-dihydrogen ligand change the properties of this interesting ligand.[1-6] Only small changes were observed in early

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