

Supplementary information: EQCM Analysis of Redox Behavior of Prussian Blue in a Lithium Battery Electrolyte

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Detailed experimental results related to the electrodeposition of Prussian blue thin films

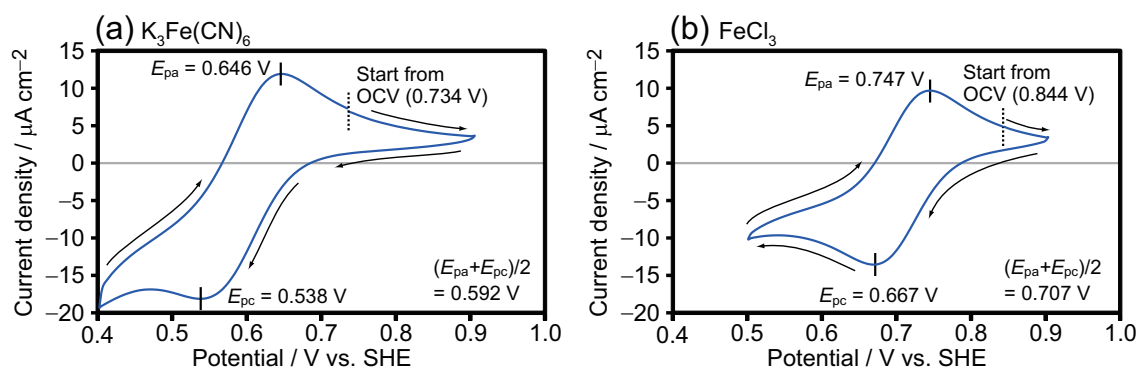


Fig. S1 Cyclic voltammograms (2nd cycle) measured at 10 mV s^{-1} in aqueous solutions (pH *ca.* 1) containing (a) 1.0 mM $\text{K}_3\text{Fe}(\text{CN})_6$, 1.00 M NaCl and (b) 1.0 mM FeCl_3 , 1.00 M NaCl. Anodic and cathodic peak potentials (E_a and E_c) and the mean of the two peak potentials ($\frac{E_a+E_c}{2}$) are also indicated.

Fig. S1 shows cyclic voltammograms measured in aqueous solutions (pH *ca.* 1) containing 1.0 mM $\text{K}_3\text{Fe}(\text{CN})_6$ or FeCl_3 . Assuming that the following redox reactions



are both reversible, the redox potentials of $\text{Fe}^{\text{III}}(\text{CN})_6^{3-}/\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ are close to the means of the cathodic and anodic peak potentials ($\frac{E_a+E_c}{2}$), *i.e.* about 0.59 and 0.71 V vs. SHE, respectively. These values are slightly different from the reported values (see Table S1) because the reported values were determined under standard conditions (activities of all the chemical species are 1); the electrolytes used here

Table S1 Determined and reported redox potentials of $\text{Fe}^{\text{III}}(\text{CN})_6^{3-}/\text{Fe}^{\text{II}}(\text{CN})_6^{2-}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couples.

Redox couple	Redox potential (Determined)	Standard redox potential (Reported) ¹
	/V vs. SHE	/V vs. SHE
$\text{Fe}^{\text{III}}(\text{CN})_6^{3-}/\text{Fe}^{\text{II}}(\text{CN})_6^{2-}$	+0.592	+0.36
$\text{Fe}^{3+}/\text{Fe}^{2+}$	+0.707	+0.771

Table S2 EDX analysis results for PB film deposited at 0.6 V vs. SHE for 5 min from an aqueous solution (pH ca. 1) containing 1.0 mM $\text{K}_3\text{Fe}(\text{CN})_6$, 1.0 mM $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 0.10 M HCl, and 1.00 M NaCl.

Element	Fe	C	N	Na	K	Cl
at. %	3.5	39.4	57.1	0.0	0.0	0.0

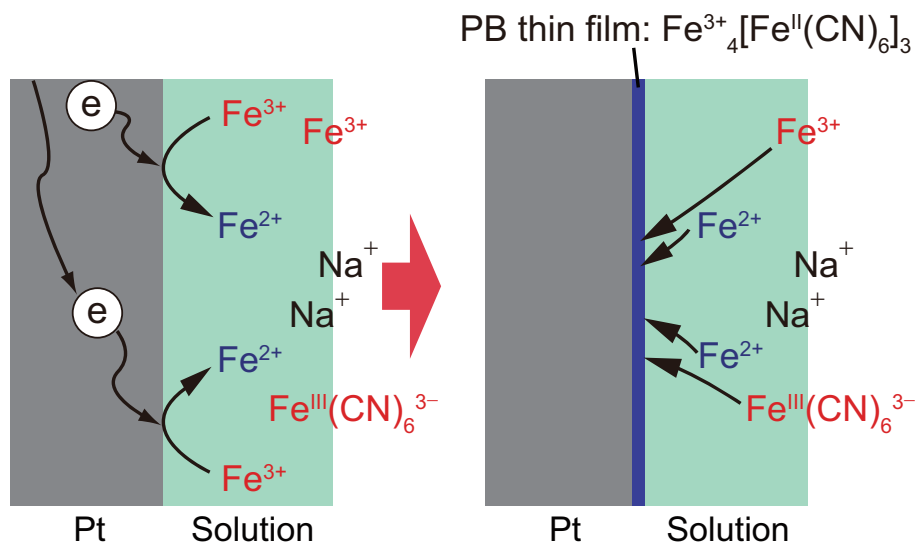
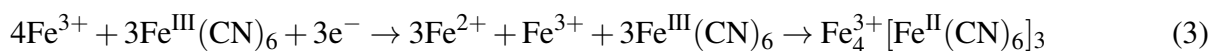


Fig. S2 Schematic illustration of the deposition behavior of a PB thin film under the present condition.

initially contained only single iron species (1.0 mM Fe^{3+} ions or 1.0 mM $\text{Fe}^{\text{III}}(\text{CN})_6^{3-}$), and the conditions differed from the standard conditions. Thus, under the present electrodeposition conditions (at 0.6 V vs. SHE), Fe^{3+} aquo ions are mainly reduced to form Prussian blue (PB) by combining with $\text{Fe}^{\text{III}}(\text{CN})_6^{3-}$ and unreduced Fe^{3+} ions. The EDX analysis result of the deposited PB film is shown in Table S2. Although the quantitative accuracy of EDX for light elements such as C and N is poor, the present results clearly indicate that the PB film did not contain Na, K, and Cl elements and was mainly composed of only Fe, C, and N elements. It should be noted that PB (ferric ferrocyanide) and Turnbull's blue (ferrous ferricyanide) are identical ($\text{Fe}_4^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]_3$), and the electrodeposition of PB proceeds through the electron transfer from Fe^{2+} aquo ions with the high spin state to Fe(III) in $\text{Fe}(\text{CN})_6^{3-}$ with the low spin state or flipping of the ligand CN^- by 180° as follows:^{2,3}



Obviously, the deposition behavior will change with the deposition conditions, specifically the kind and concentration of dissolved species and deposition potential. The deposition behavior of the PB thin film under the present conditions is summarized in Fig. S2

Fig. S3 shows the weight change of a Pt-sputtered quartz crystal substrate during the electrodeposition of a Prussian blue (PB) thin film. The total weight of the deposited PB was about $9.6 \mu\text{g}$ at 5 min and $12.6 \mu\text{g}$ at 10 min. The decrease in the absolute value of the cathodic current density suggests the electrodeposition of the PB thin film with a high electrical resistance.

Fig. S4 shows the change in resonance resistance of a PB-deposited quartz crystal substrate during the

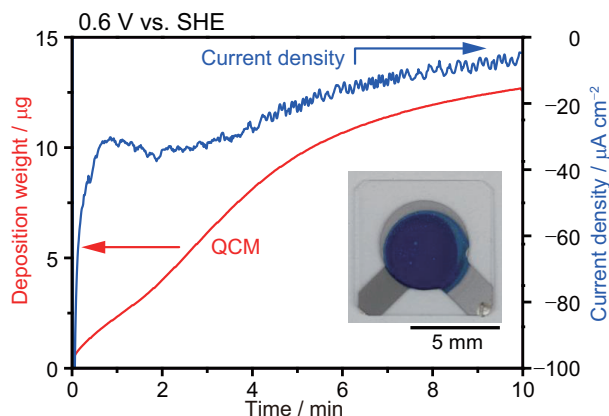


Fig. S3 Change in weight and current density during the electrodeposition of PB thin film at 0.6 V vs. SHE for 10 min. (d) Schematic illustration of the deposition behavior of a PB thin film.

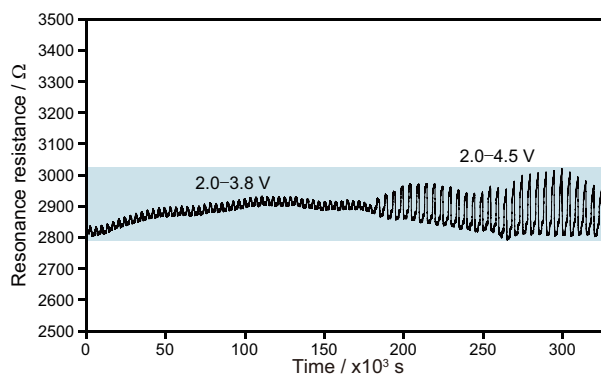


Fig. S4 Change in resonance resistance of the quartz crystal substrate on which a PB thin film was deposited at 0.6 V vs. SHE for 10 min during cyclic voltammetry for 50 cycles from 2 to 3.8 V and subsequent 30 cycles from 2 to 4.5 V vs. Li/Li⁺ at 1 mV s⁻¹ in 1 M LiPF₆ EC-DMC (1:2 by vol.).

cyclic voltammetry corresponding to the result of Fig. 3 in the manuscript. The resonance resistance was stable enough during each cycle and well reflected the changes in viscosity and density of the electrolyte in the vicinity of the substrate because of the changes in ion concentrations.⁴ Although the amplitude was intensified during the cyclic voltammetry from 2 to 4.5 V vs. Li/Li⁺ mainly due to the electrolyte decomposition above 4.2 V, the resonance frequency was relatively stable in the range from 2790 to 3020 Ω. Thus, the weight change of the PB-deposited QCM substrate was estimated from the change in resonance frequency using Sauerbrey equation in the present paper.

References

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