

Electrochemical cation adsorption/desorption control of nanoparticle film of Prussian blue type complexes

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Abstract

Since Prussian blue (PB, or FeHCF) and its analogues [PBA or MHCF (M = Ni, Zn, Co, Cu, etc.)] are well known as adsorbents of some ions or small molecules, especially, alkali metal cations such as Na⁺, K⁺ and Cs⁺, these materials had been regarded as promising adsorbents to remove a radioactive Cs⁺ from radioactive wastes. However, to adsorb a radioactive Cs⁺ with MHCF causes the increase of radioactive wastes, so it is important to develop a reusable new system, or a controllable Cs⁺ adsorbing/desorbing system. We succeeded in preparing nanoparticle inks of MHCF, which are able to disperse into several solvents, and able to form films with the nanoparticle inks by conventional wet processes. Then we prepared the CuHCF nanoparticle films on Au/quartz substrates by a spin-coating method, and attempted to control the adsorption or desorption of alkali metal cations electrochemically. The electrochemical redox by cyclic voltammetry (CV) and adsorption/desorption measurement by electrochemical quartz crystal microbalance (EQCM) were carried out synchronously. For example, a copper substituted PBA, CuHCF films showed stable reversible redox signals for Na⁺, K⁺ and Cs⁺ in the aqueous solution dissolving the corresponding nitrate salts (NaNO₃, KNO₃ and CsNO₃) as electrolytes. The redox potentials were different to each other, +0.55 V, +0.65 V, and +0.90 V (vs. SCE) for Na⁺, K⁺ and Cs⁺, respectively. According to EQCM measurement, the mass changes followed by a cation adsorption/desorption occurred at the above-described potentials respectively and the ratios of mass showed almost 1:1:6 for Na⁺:K⁺:Cs⁺. The difference of redox potentials and good duplicability of CV and EQCM signals suggests the possibility of electrochemically controllable cation adsorbing/desorbing systems.

Introduction

The radioactive caesium such as ^{137}Cs ($T_{1/2} \sim 30.1$ years) is one of heat sources in radioactive wastes. As a means of removing the radioactive nuclide, extensive studies have been done using hexacyanoferrates (HCF). A variety of metal hexacyanoferrates (MHCF) have been reported, that have a selective affinity for Cs^+ over a wide pH range and good resistance to radiation [1-4]. However, the Cs^+ adsorption to bulk MHCF is the reaction occurred at the interface between solid and liquid, so it takes a good amount of time to diffuse and adsorb the cation. Additionally, the regeneration of the adsorbed MHCF is not so easy. It often needs chemical treatments for pH control, so additional chemical reagents are consumed and that increases the total amount of wastes.

In this paper, we report the Cs^+ adsorption using nanoparticle inks of MHCF. Since this is a liquid-liquid reaction (strictly saying, reaction occurred at the interface between water-dispersing nanoparticle surface and liquid), more rapid adsorption is expected. And after adsorption, as nanoparticles of MHCF become insoluble and form precipitates, it is also expected to be easy to separate. Moreover, to achieve a sustainable recycling system of Cs^+ recovering, we try to perform the electrochemical control of alkali metal cations adsorption/desorption using MHCF nanoparticle films coated on electrodes. The electrochemical separation of cations were reported using electrodeposited thin films of MHCF [5,6]. However, to raise the efficiency of separation, it is necessary to increase the effective volume and surface area of MHCFs on electrodes.

Experimental

Water-dispersible nanoparticle inks of $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ (FeHCF) and $\text{Ni}_3[\text{Fe}(\text{CN})_6]_2$ (NiHCF) were synthesised by the method reported in our previous paper [7]. The insoluble core of $\text{Cu}_x[\text{Fe}(\text{CN})_6]$ (CuHCF) was synthesised by the arrangement procedure of the paper [8], and the surface modification (water-dispersible process) was carried out based on that of FeHCF [7]. According to Refs. [8,9], several compositions of insoluble $\text{Cu}_x[\text{Fe}(\text{CN})_6]$ (CuHCF) can be prepared, such as $x = 1, 1.5, 2$. We mainly chose the $x = 2$ salt, $\text{Cu}_2[\text{Fe}(\text{CN})_6]$, because of its good adsorption property of Cs^+ .

Water-dispersible $\text{Cu}_x[\text{Fe}(\text{CN})_6]$ (CuHCF) nanoparticle ink

Insoluble nanoparticle of $\text{Cu}_x[\text{Fe}(\text{CN})_6]$ was prepared by mixing an aqueous solution of Cu^{2+} and hexacyanoferrate anion. For example, in case of $x = 2$, an aqueous solution (5 ml) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1.36 g, 8.0 mmol) was added to an aqueous solution (5 ml) of $\text{Na}_4[\text{Fe}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$ (1.94 g, 4.0 mmol). The reaction mixture was vigorously shaken by hand for 5 min. The precipitated $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ was separated by a centrifuge machine, and washed with deionised water five times. Then, the precipitate was dispersed in 40 ml deionised water and added $\text{Na}_4[\text{Fe}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$ (0.58 g, 1.2 mmol) as a surfactant. After stirring for four days, a dark red ink of water-dispersible CuHCF was prepared. From an energy dispersive X-ray spectroscopy (SEM-EDX, Hitachi S-3500N, Horiba EMAX300) measurement, the Cu/Fe ratio was estimated at 1.7(1). In case of $x = 1.5$, $\text{Cu}_3[\text{Fe}(\text{CN})_6]_2$ salt, an aqueous solution (5 ml) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1.53 g, 9.0 mmol) was added to an aqueous solution (5 ml) of $\text{K}_3[\text{Fe}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$ (1.98 g, 6.0 mmol). The following process was almost same, but 0.73 g of $\text{Na}_4[\text{Fe}(\text{CN})_6] \cdot 10\text{H}_2\text{O}$ (1.2 mmol) was used for a surfactant.

In this paper, the description of “CuHCF” means $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ if there is no notice. In case of necessity to distinguish between different compositions, it is described as CuHCF1.5 for $\text{Cu}_3[\text{Fe}(\text{CN})_6]_2$ and CuHCF2 for $\text{Cu}_2[\text{Fe}(\text{CN})_6]$.

Cs^+ adsorption with FeHCF or CuHCF inks

The sample solutions for Cs^+ adsorption were prepared by dissolving caesium nitrate as desired proportions in distilled water, about 100 ppb for FeHCF and 10 ppb for CuHCF. Each pH/acid concentration was adjusted by adding nitric acid and determined by pH meter or potentiometric titrator. 50 mg of FeHCF or CuHCF dried ink was added in 2.0 ml of the sample solutions and

stirred for 3 hours. The FeHCF or CuHCF nanoparticles immediately dispersed in solution, then adsorbed Cs^+ , and settled out of solutions. The adsorbed MHCF were separated by filtration. The Cs^+ concentrations in the solution before and after adsorption were measured by ICP-MS Spectrometer (Seiko Instruments Inc., SPQ-9800).

Electrochemical adsorption/desorption of alkali metal cations with CuHCF inks

For the electrochemical adsorption or desorption control of alkali metal cations, the thin film of CuHCF was formed on the Au/quartz electrode by a spin-coating method using water-dispersible nanoparticle ink of CuHCF (0.5 g/ml). After heating at 100°C for 2 hours, the spin-coated film became insoluble. Thus, the electrochemical property could be measured in the aqueous solution of 0.1 M alkali metal nitrate (CsNO_3 , KNO_3 and NaNO_3) as electrolyte, with a saturated calomel electrode (SCE) as a reference electrode and a Pt wire as a counter electrode. The film thickness was estimated at 300-400 nm from a stylus-type surface profilometer measurement (Alpha-step IQ; KLA Tencor Corp.). A cyclic voltammetry (CV) measurement was performed with potentiostat/galvanostat (Princeton Applied Research, 263A), and an electrochemical quartz crystal microbalance (EQCM) measurement was simultaneously done with a quartz crystal analyser (Princeton Applied Research, QCA922).

After electrochemical treatments with each cations, the elemental analysis of alkali metal compositions in the thin film of CuHCF was measured with SEM-EDX (Hitachi S-3500N, Horiba EMAX300). Three thin films of CuHCF on Au/Ti/glass substrates were prepared by a spin coating. The electrochemical measurement was performed in the mixture electrolyte of 0.1 M CsNO_3 , KNO_3 and NaNO_3 solution at equal amount of volume. After applying cyclic potential sweep between 0 V and +1.5 V for 10 cycles, applying 0 V for 2 sec for initialising, each CuHCF film was applied the potential +0.3 V, +0.8 V, and +1.2 V for 60 sec, respectively. Cleaning the surface by air blow, then the elemental analysis was measured with SEM-EDX.

Results and discussion

Cs^+ adsorption with FeHCF or CuHCF inks

As mentioned above, MHCF salts have been known as good adsorbents of alkali metals. Therefore, the adsorptive property of insoluble bulk MHCF salts has been studied for more than 50 years [1-4]. However, the cation adsorption to the bulk materials was dominated by the cation diffusion in solution, so it generally takes a good amount of time. Compared with such bulk materials, the nanoparticle materials has much large surface area and that ink is well mixed with the sample solution, so it is expected to be better adsorptive activity. In Table 1, the results of Cs^+ adsorption with FeHCF and CuHCF inks are listed at various acidity conditions. As soon as the FeHCF dropped into the sample solution and stirred, a dark blue precipitate was formed. After filtering the colloid solution, the Cs^+ concentrations in the filtrate were below the limit of detection. Therefore, the distribution coefficients (K_d) were more than 1 000 even in high acidity condition, such as 0.5 M. In case of CuHCF ink, a dark orange precipitate was formed by dropping CuHCF into the sample solution. It took several hours to settle down. After filtration, the Cs^+ concentrations in the filtrate were also around the limit of detection in the wide range of acidity. These results indicate that the FeHCF and CuHCF inks have high adsorptive activity with rapid reaction. The adsorbed MHCFs form precipitate immediately, while the surplus MHCFs disperse in solution. Therefore, the MHCF including Cs^+ can be easily removed from the solution.

Electrochemical adsorption/desorption of Alkali metal cations with CuHCF inks

Although the good Cs^+ adsorptive ability of CuHCF ink became clear by the adsorption experiment, only an adsorption is not enough for sustainable recovery systems. It is necessary to repeat adsorption and desorption. Therefore, we tried to make the adsorption and desorption of Cs^+ on CuHCF film electrochemically. Additionally, Na^+ and K^+ adsorption/desorption experiments were carried out to clear the selectivity among alkali metal cations. The CV and EQCM measurements

Table 1: Cs⁺ adsorption with FeHCF and CuHCF inks

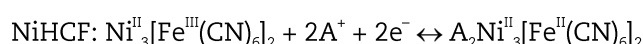
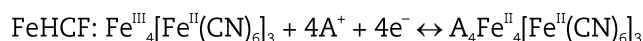
Sample	Initial pH/ acid concentration (M)	Cs initial concentration (ppb)	Cs final concentration (ppb)	K _d
FeHCF	pH 4.70	96.95	0.000	> 1 000
	pH 2.25	95.98	0.000	> 1 000
	pH 1.25	95.01	0.000	> 1 000
	0.1 M	101.29	0.000	> 1 000
	0.2 M	95.54	0.000	> 1 000
	0.5 M	101.43	0.000	> 1 000
CuHCF	pH 7.00	9.24	0.018	10 207
	pH 2.25	9.79	0.012	16 689
	pH 1.25	10.37	-0.027	>10 000
	0.1 M	9.59	0.010	19 195
	0.2 M	9.93	0.001	149 506
	0.5 M	9.40	0.030	6 268

of CuHCF thin film with CsNO₃, KNO₃, and NaNO₃ as electrolyte were shown in Figure 1. Each cyclic voltammogram showed a stable reversible redox signal at different potentials, at +0.55 V (NaNO₃), +0.65 V (KNO₃), and +0.90 V (CsNO₃), respectively. The reproducibility of the redox showed little change, at least, within 100 cycles. According to the CV, the total charges needed for the adsorption/desorption of these cations were almost equal. However, the ratio of D mass was estimated at 6:1:1 for CsNO₃, KNO₃ and NaNO₃ according to the EQCM. It is close to the relative atomic mass ratio of Cs, K and Na, 5.7:1.7:1. These results suggested that the nanoparticle film of CuHCF was a good adsorbent of alkali metal cations and could separate the cations by the electrochemical treatment.

As compared with the CuHCF film, the results of CV measurement of NiHCF were shown in Figure 2. In the case of NiHCF, although the reversible redox curves were observed in Cs⁺, K⁺ and Na⁺, the peaks of Cs⁺ shrank gradually. After 10 cycles potential sweep, the intensity of CV peak with Cs⁺ was less than 1/5, and the redox potential was around +0.5 V, which is almost overlapped with the peak of K⁺.

To demonstrate the electrochemical adsorption/desorption property and separability of CuHCF, the elemental analysis with SEM-EDX was performed on CuHCF films applied potentials. The atomic ratio was tabulated in Table 2, applying potential at +0.3 V, +0.8 V and +1.2 V. The Cu/Fe ratios were 1.7(1)-1.8(1), which were smaller than those of expected, 2.0. Initially, the CuHCF film contained Na⁺, which came from Na₄[Fe(CN)₆]. After applying cyclic potential sweep between 0 V and +1.5 V for 10 cycles in the mixed electrolyte of 0.1 M CsNO₃, KNO₃ and NaNO₃ at equal amount of volume, the CuHCF film was applied the potential +0.3 V, +0.8 V and +1.2 V, as shown by arrows in Figure 1. It is indicated that the alkali metal cations adsorption/desorption was controlled by electrochemically, or the Na⁺/K⁺/Cs⁺ ratios in the CuHCF films were controlled by applied potentials.

The electrochemical alkali metal cation (A⁺) adsorption/desorption of FeHCF and NiHCF are known as follows:



The redox of CuHCF1.5 is same as NiHCF, however, the electrochemical cation adsorption/desorption mechanism of CuHCF2 is not clear:

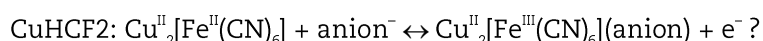
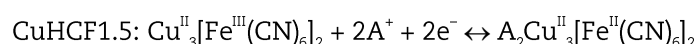
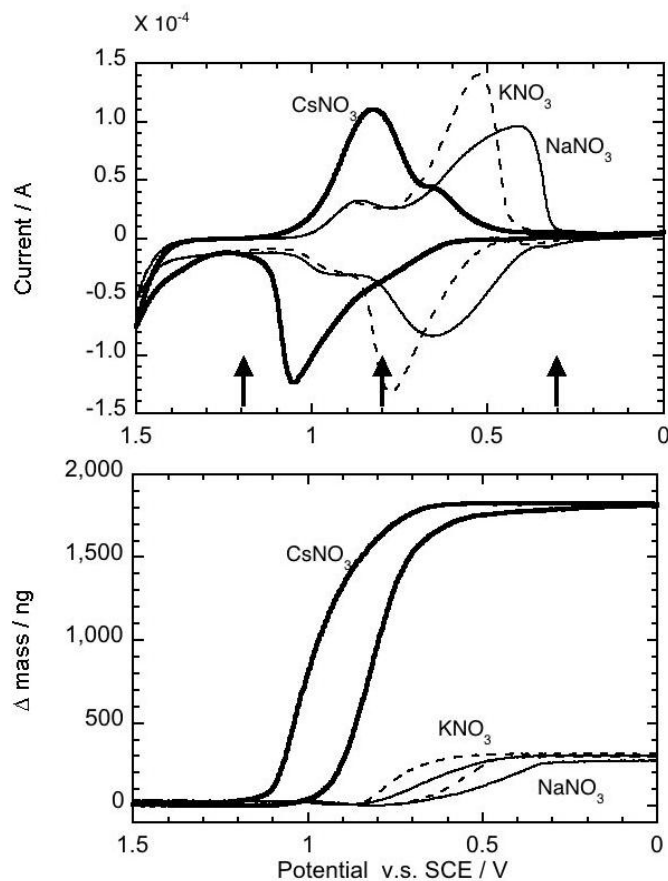


Figure 1: CV (top) and EQCM (bottom) measurements of CuHCF thin film

The vertical axis of EQCM was transformed from frequency to mass change (Δ mass). Scan rate was 20 mV/sec. The arrows mean +0.30, +0.80 and +1.20 V, which are explained in Table 2.

**Figure 2: CV measurement of NiHCF thin film**

The curves here were 10th cycle data. Scan rate was 20 mV/sec.

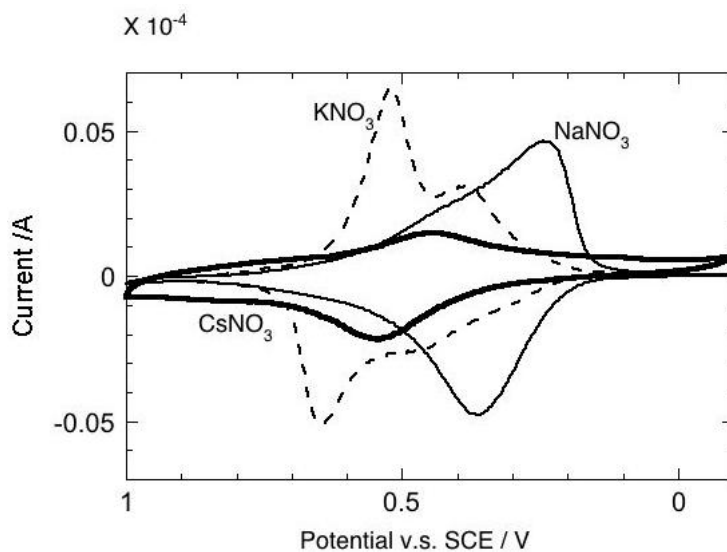


Table 2: Atomic ratio of CuHCF films with SEM-EDX

The ratio is normalised by Fe atom

	Initial composition	+0.3 V	+0.8 V	+1.2 V
Fe	1	1	1	1
Cu	1.8 (1)	1.7 (1)	1.8 (1)	1.7 (1)
Na	1.1 (2)	0.30 (1)	0.0	0.0
K	0.30 (5)	0.41 (5)	0.21 (10)	0.16 (2)
Cs	–	1.09 (10)	0.82 (6)	0.31 (2)

The adsorption kinetics of copper hexacyanoferrate were discussed in several papers [8-10]. The reported crystal structure of CuHCF1.5 is cubic, $Fm\bar{3}m$. The co-ordinations between Cu and $\text{Fe}(\text{CN})_6$ formed cubic frameworks [8]. On the other hand, the crystal structure of CuHCF2 is similar to those of CuHCF1.5, however, certain of Cu atoms occupy the $(1/4\ 1/4\ 1/4)$ position of cubic, but not framework site. Ayaraut, et al. reported that the maximum uptake of CuHCF1.5 is 0.073 Cs/Fe, while that of CuHCF2 reaches 1.5 Cs/Fe [8]. However, the preliminary experiment detected no obvious difference between CuHCF1.5 and CuHCF2, at least for the electrochemical adsorption/desorption property. From our SEM-EDX result ($\text{Cu/Fe} = 1.7\text{-}1.8$), our CuHCF seems to contain no small amount of CuHCF1.5, which works as the electrochemical adsorption/desorption of alkali metal cations.

In conclusion, the adsorption/desorption control of alkali metal cations was performed electrochemically with nanoparticle inks of MHCF. According to the CV and EQCM measurement of CuHCF film, the reversible redox waves and mass changes were observed, and the redox potentials of the film in Cs^+ , K^+ and Na^+ were separated each other. The results suggested that, for example, Cs^+ could be removed from waste solution and recovered repeatedly by electrochemical control. The system is simple, compact (it needs a pot, a potentiostat, electrodes and small space) and sustainable (low-energy-consuming and repeatedly available). Therefore, the electrochemical Cs^+ recovery using CuHCF nanoparticle seems to be one of prospective systems.

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