

Lithium intercalation behavior of iron cyanometallates

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Abstract

Iron cyanometallates having a formula, $M_{6-m}^{n+}[Fe^{m+}(CN)_6]_n$ ($M = V, Mn, Co, Ni, Cu$) were prepared and their charge–discharge behavior was discussed. In the V–Fe complex, average discharge potential is about 3.6 V corresponding to reduction of V^{3+} , whereas the Mn, Co, Ni, and Cu complexes show similar discharge potential around 3.3 V that is resulted from reduction of $[Fe^{3+}(CN)_6]^{3-}$ unit in the lattice. The specific capacity of V, Mn, Co, Ni complexes show about 60–80 mA h g^{-1} , but copper complex indicates almost double capacity, ca. 140 mA h g^{-1} . This is explained by considering the capacity caused by Cu^{2+} to Cu^+ reduction in addition to $[Fe^{3+}(CN)_6]^{3-} \rightarrow [Fe^{2+}(CN)_6]^{4-}$ reduction. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

There are increasing interests in secondary lithium batteries consisting of intercalation compounds for both the cathode and anode, in accordance with the development of portable electronic equipment, and as a power supply for future electric vehicles and load leveling systems. The focus of this study is to adopt an iron containing material to the cathode of a lithium secondary battery which is favorable for the cost and environmentally acceptable. Prussian blue is one of the best known examples in multinuclear cyanometallate system and is also known as an electrode of electrochromic display [1–4]. Prussian blue is an iron mixed-valence hexacyanometallate described as $Fe_4^3+[Fe^{2+}(CN)_6]_3$, in which metal cyanide units and metal cations combine together to form three dimensional polymeric frameworks [5,6]. It has open spaces due to the large asymmetric CN^- anion, and they connect each other to form a tunnel structure, which can accommodate not only neutral molecules but charged species balanced by the iron valence state. The authors have studied this material as cathode of lithium battery and found that it can accommodate lithium ions reversibly from aprotic solvents, which is not possible from aqueous solution. As a lithium battery

cathode, average voltage of 3 V and capacity of 110 mA h g^{-1} are the best results which we obtained in the course of study.

Another interesting feature of the material is that part of iron ions in $Fe_4^3+[Fe^{2+}(CN)_6]_3$ can be readily replaced by other transition metals. This leads to wide varieties of materials and physical properties, e.g., magnetic properties [7–9]. In this study, we try to check the possibility of these analogues as cathode of lithium battery. As a substituent, V, Mn, Co, Ni and Cu were selected and systematic study in cyanometallates that has a formula, $M_{6-m}^{n+}[Fe^{m+}(CN)_6]_n$ was attempted.

2. Experimental

Prussian blue analogues were prepared by the following method. All cases except for vanadium, MCl_2 ($M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}$) and $K_3[Fe(CN)_6]$ were separately dissolved in deoxygenated distilled water, then mixed in 3:2 molar ratio at room temperature. In case of vanadium, VCl_3 and $K_4[Fe(CN)_6]$ were reacted. In every case, colored precipitate immediately occurred and the suspension was stirred for a couple of hours to mature. After repeated centrifuging and washing in a distilled water, it was dried at 60°C for 1 week in air, then vacuum dried at 60°C for 24 h. Only copper–iron cyanocomplex was dried at 40°C because of its low thermal stability. All the samples were

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Table 1

The mole ratio of substitutive metal cations (V, Mn, Co, Ni, Cu) and iron in each complex determined by ICP measurements

	V	Mn	Fe	Co	Ni	Cu
$V^{3+}-Fe^{2+}$	1.28		1			
$Mn^{2+}-Fe^{3+}$		1.52	1			
$Co^{2+}-Fe^{3+}$			1	1.56		
$Ni^{2+}-Fe^{3+}$			1		1.61	
$Cu^{2+}-Fe^{3+}$			1			1.51

For simplicity, the number of iron is fixed at 1.0.

stored in a sealed glass tube in order not to change the degree of hydration.

Powder X-ray diffraction (XRD) measurements were carried out at the scanning speed of $0.5^\circ \text{ min}^{-1}$ by a Rigaku Rotaflex diffractometer with monochromated $\text{CuK}\alpha$ radiation at 40 kV, 150 mA. During the measurements, samples were kept in an argon atmosphere to avoid moisture. The mole ratio of substitutive metal cation and iron was determined by inductively coupled radio frequency plasma (ICP) flame analysis by dissolving reaction products in a concentrated HCl solution. The measurements were carried out using Shimadzu ICPS-1000IV, in which yttrium was added to the test solutions as an internal standard element. The Mössbauer effect of ^{57}Fe was performed at room temperature. The velocity was calibrated by using pure iron metal as a standard material.

A button cell was used to measure the electrochemical properties of the complex cathodes. It has an identical dimension to a commercial CR2025 cell, of which the upper and lower sides are 20 mm in diameter and the total thickness is 2.5 mm. The cathodes were prepared by mixing iron complex powder with acetyleneblack conduc-

tive agent (20 wt.%), and polytetrafluoroethylene binder (0.1 wt.%). The mixture was pressed into a disc-shape and put on a stainless steel mesh working as a current collector. Consequently a cathode tablet having about 1 mm thickness was obtained. A lithium metal sheet was used as the anode and put on the counter side to the cathode. A non-woven fabric of polypropylene was used as a separator soaked with one molar solution of LiClO_4 in a propylene carbonate/1,2-dimethoxy ethane mixture. The cell was assembled in a dry argon filled glove box. The charge–discharge cycling tests of these cells were carried out between 2.5 and 4.3 V cut-off voltages at a constant current density of 0.1 mA cm^{-2} .

3. Results and discussion

The mole ratio of substitutive metal and iron in each complex determined by ICP measurements are listed in Table 1. For $M = \text{Mn, Co, Ni, and Cu}$, the mole ratio is about 1.5 (3/2). This means a chemical formula of the products is $M_3[\text{Fe}(\text{CN})_6]_2$, if a single phase is produced. In the case of vanadium, the mole ratio of V and Fe is close to 1.33 (4/3). A chemical formula of the product is described as $V_4[\text{Fe}(\text{CN})_6]_3$. These ICP results imply that the valence state of each metal in the prepared cyanocomplex is principally same as that of starting crude materials.

XRD patterns of the prepared cyanocomplexes are shown in Fig. 1. All the samples have the same pattern showing a crystal symmetry of the space group $Fm\bar{3}m$ with a face-centered cubic unit cell. For $M = \text{V, Mn, Ni, and Cu}$, a single phase appears, but Co–Fe sample has a small amount of impurity of which peaks are marked by a

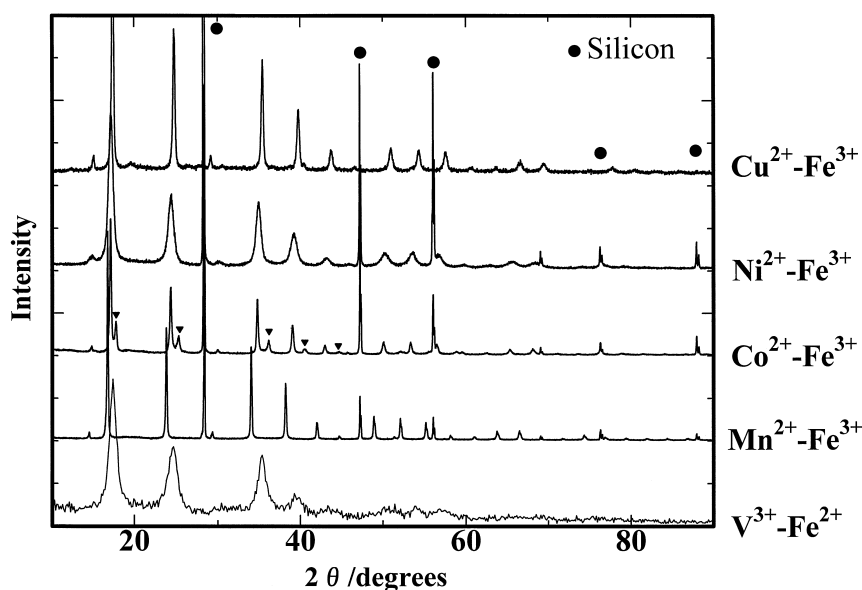


Fig. 1. XRD patterns of the prepared cyanometallates. The kind of the substitutive metal is shown on the right of the figure. The triangle mark in the Co–Fe pattern indicates an impurity phase.

triangle. This impurity also has a cubic lattice with a smaller lattice parameter. The calculated lattice parameters from XRD data is $a = 10.19(1) \text{ \AA}$ for $V_4[Fe(CN)_6]_3$, $a = 10.525(3) \text{ \AA}$ for $Mn_3[Fe(CN)_6]_2$, $a = 10.307(3) \text{ \AA}$ for $Co_3[Fe(CN)_6]_2$, $a = 10.269(6) \text{ \AA}$ for $Ni_3[Fe(CN)_6]_2$, and $a = 10.150(3) \text{ \AA}$ for $Cu_3[Fe(CN)_6]_2$. In the 3:2 complex, the lattice parameter is decreasing with the increase of the atomic number of the substitutive metal. It is also in the same order as the ionic radius of these divalent cations. Considering the high ionicity of these cations in the complex lattice, it is rational to assume the lattice parameter is

controlled by the ionic size of substituent. $V_4[Fe(CN)_6]_3$ shows a much smaller lattice parameter, but it is due to the different type of composition and comparable to that of Prussian blue, $10.158(3) \text{ \AA}$ which has the same type of chemical formula.

Mössbauer spectra were measured to clarify the valence state of iron contained in the complex and the results are shown in Fig. 2. The isomer shifts are always located at zero or below. This indicates strong covalency of the bond between iron and its surrounding strong ligands CN^- and consequently d-electrons of iron are arranged in low

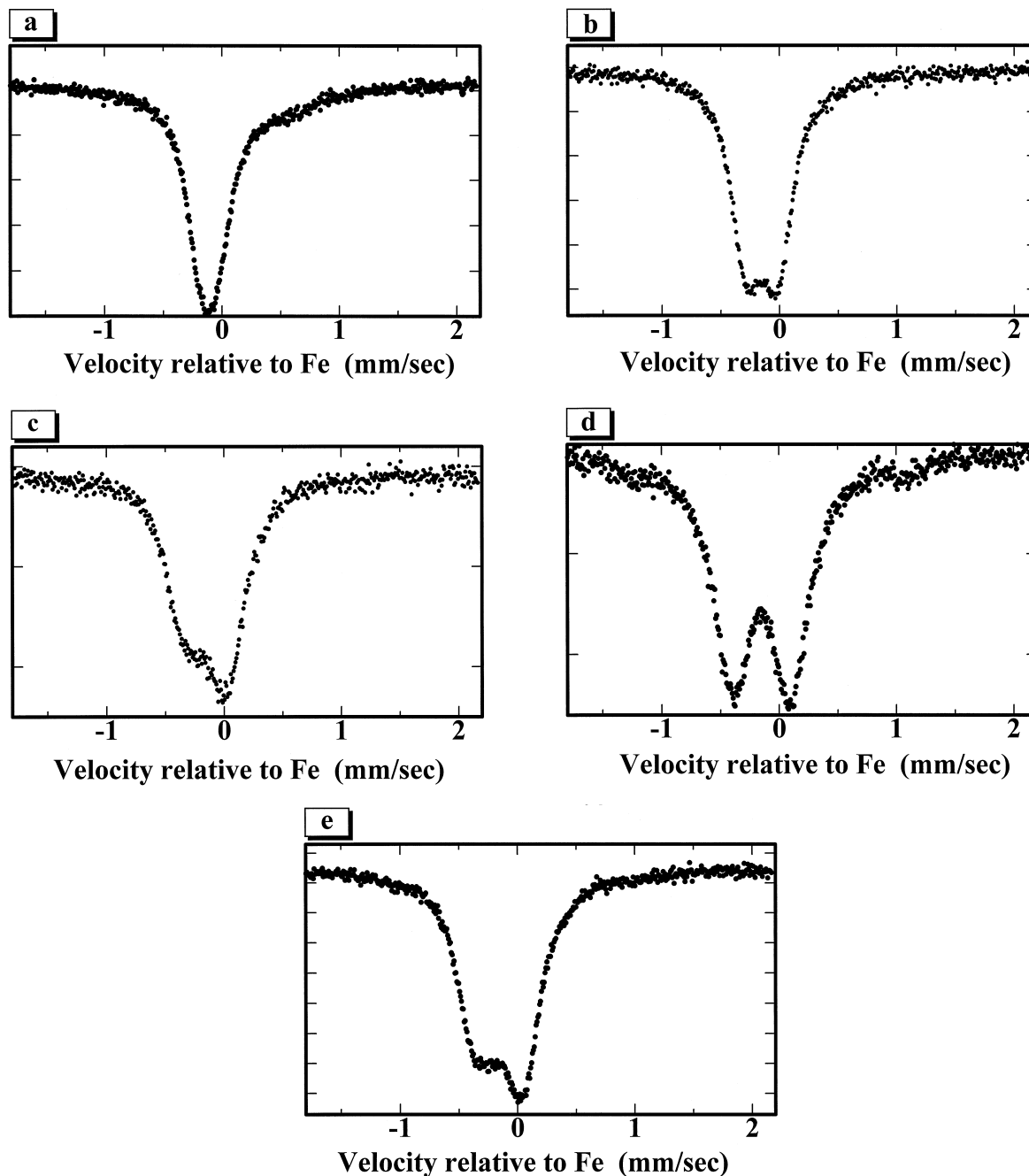


Fig. 2. Mössbauer absorption spectra of the prepared cyanometallates at room temperature. a: V–Fe, b: Mn–Fe, c: Co–Fe, d: Ni–Fe, e: Cu–Fe.

spin state. This analysis supports the chemical formula $M_3[Fe(CN)_6]_2$ or $M_4[Fe(CN)_6]_3$ suggested from the ICP measurements. In the case of V–Fe complex, the spectrum indicates a singlet at 0 mm s^{-1} indicating low spin Fe^{2+} is only contained. Mn–Fe and Ni–Fe complex show a doublet of which isomer shift is located at ca. -0.2 mm s^{-1} and low spin Fe^{3+} is confirmed for these two complexes. The different degree of quadrupole splitting reflects deviation from sphere symmetry of circumstance around iron in the Ni–Fe complex. In the case of Co–Fe complex, asymmetric doublet appears. This is possibly because of overlapping low spin Fe^{3+} doublet and small low spin Fe^{2+} singlet. The origin of Fe^{2+} can be assigned to the impu-

urity, which is observed in the XRD pattern. The Cu–Fe complex also shows asymmetric doublet, although there are no peaks of impurity in the XRD pattern. In this case, the complex is a single phase, but part of Fe^{3+} is reduced to Fe^{2+} , which is compensated by intercalation of potassium. It should be noted that Cu^{2+} is a strong Jahn–Teller ion, while $Fe^{3+}(CN)_6^{3-}$ is isotropic. It is not difficult to imagine that construction of a stable cubic lattice by an alternative combination of symmetric and asymmetric units. This consideration is partly supported by the fact that the Cu–Fe complex easily decomposes by heating compared to others. The reduction to Fe^{2+} leads to the extra electron staying at Cu^{2+} ion and the distortion may be relaxed

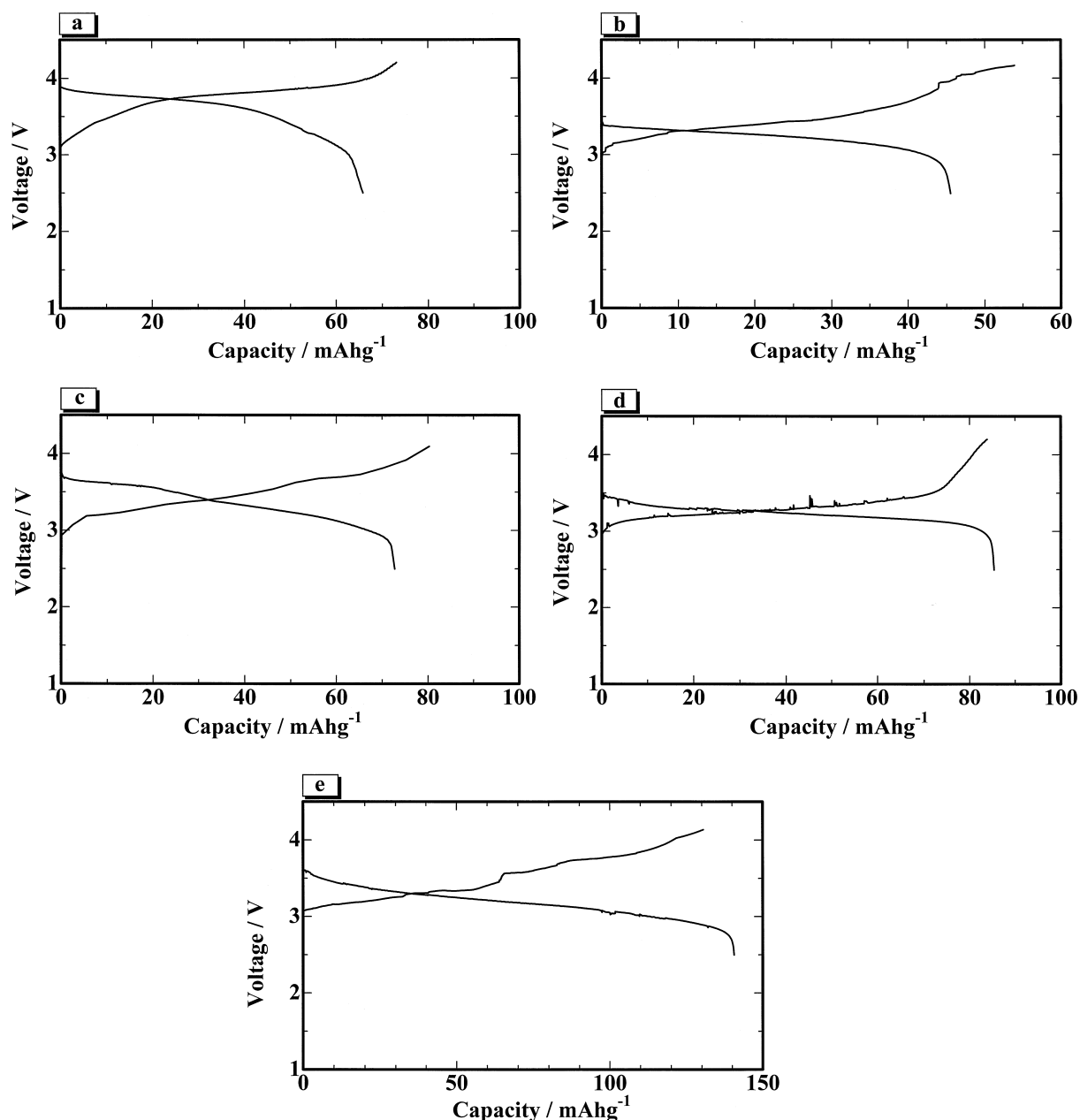


Fig. 3. Charge–discharge behaviors of the cyanometallates in the first cycle at a constant current density of $100 \mu \text{ cm}^{-2}$. a: V–Fe, b: Mn–Fe, c: Co–Fe, d: Ni–Fe, e: Cu–Fe.

enough to build a lattice. From these characterizations, final chemical formula of the products are revealed as $V_4^{3+}[Fe^{2+}(CN)_6]_3$, $Mn_3^{2+}[Fe^{3+}(CN)_6]_2$, $Co_3^{2+}[Fe^{3+}(CN)_6]_2$, $Ni_3^{2+}[Fe^{3+}(CN)_6]_2$, and $Cu_3^{2+}[Fe^{3+}(CN)_6]_2$.

Charge–discharge behaviors of these cyanocomplexes are shown in Fig. 3. There is a systematic change in their voltages and capacities by different transition metal replacement to the Prussian blue host structure. In the V–Fe complex, average discharge potential is about 3.6 V, which is much higher than others. In this complex, it is a vanadium ion that can be reduced, whereas in others, $[Fe^{3+}(CN)_6]^{3-}$ unit is reduced to $[Fe^{2+}(CN)_6]^{4-}$. The different mechanism of electrochemical reaction results in the different potential profile. The standard electrode potential of a $V^{3+} \leftrightarrow V^{2+}$ redox pair in water solution is about 2.75 V vs. Li. This fact indicates that it cannot be simply applied to interpret the potential of the complex. On the other hand, the Mn, Co, Ni, and Cu complexes show similar discharge potential around 3.3 V that corresponds to reduction of $[Fe^{3+}(CN)_6]^{3-}$ unit in the lattice. Kind of substitutive metal M in the formula $M_{6-m}^{n+}[Fe^{m+}(CN)_6]_n$ does not significantly influence the electrochemical potential of complex. The potential is, therefore, governed by the redox of CN^- coordinated iron and is in good agreement with the standard electrode potential of $[Fe^{3+}(CN)_6]^{3-} \leftrightarrow [Fe^{2+}(CN)_6]^{4-}$ in aqua solution.

The capacity of these materials can be clearly divided in two groups. One contains V, Mn, Co, Ni complexes and

show about 60–80 mA h g^{-1} of specific capacity. Another is copper complex, which indicates almost double capacity, ca. 140 mA h g^{-1} . This is clearly explained by considering the capacity caused by Cu^{2+} to Cu^+ reduction in addition to $[Fe^{3+}(CN)_6]^{3-} \rightarrow [Fe^{2+}(CN)_6]^{4-}$ reduction.

From the viewpoint of battery application, copper is suitable as substitutive metal to prepare high capacity complex cathode, because free M^{3+} ion in water is very rare and if any, a combination of M^{3+} and $[Fe^{3+}(CN)_6]^{3-}$ does not usually give a precipitation except for V^{3+} – Fe^{3+} couple. In order to obtain higher potential, it seems effective to change metal in the cyanide unit, $[Fe^{3+}(CN)_6]^{3-}$ to another, e.g., $[Co^{3+}(CN)_6]^{3-}$. Based on these concepts, improvement of cathode behavior of cyanometallates will be achieved.

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