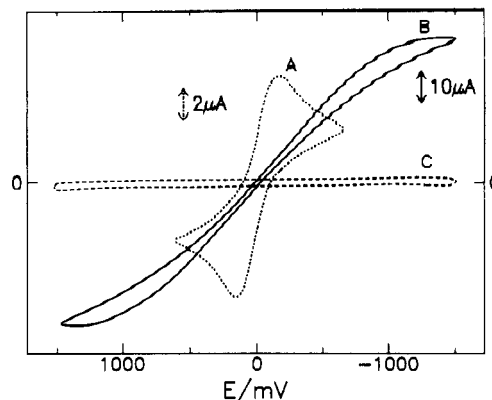


## Switching between Solid-State Electroactivity, Coupled with Ionic Conductivity, and Semiconducting or Dielectric Properties in Dry Mixed-Metal Hexacyanoferrate Powders

Transition-metal hexacyanometalates, particularly Prussian Blue and its substituted analogues, have attracted much attention in the preparation of thin electroactive films on electrodes over the past several years.<sup>1</sup> In aqueous K<sup>+</sup>-containing electrolytes, these inorganic polynuclear coatings exhibit well-defined and reversible redox behavior. A number of reports<sup>1a–d,f,j,2</sup> emphasize a special structural role for mobile potassium ions: as reductions or oxidations require transport of both electrons and ions, the stoichiometric amounts of K<sup>+</sup> (providing charge balance) change during redox transitions. The reported good ionic conductivities, intercalation capabilities, ion exchange, and zeolitic-like properties<sup>1–3</sup> should be retained in the solid state (under solvent-free conditions) as the materials are still largely hydrated upon air drying.<sup>4</sup> Simple visual tests such as homogeneous oxidation of dry Prussian White powders upon exposure to air or formation of Prussian Blue upon mixing and grinding of dry FeCl<sub>3</sub>·6H<sub>2</sub>O with K<sub>4</sub>Fe(CN)<sub>6</sub>·3H<sub>2</sub>O suggest that solid-state reactions are feasible. Recent studies with the ionically conducting polymer films using sandwich and interdigitated array electrodes<sup>1d,5</sup> are encouraging in this context. Further, transition-metal hexacyanoferrates are Robin and Day's class II mixed-valence compounds<sup>6</sup> that show semiconducting characteristics. The actual electrical conductivity is dependent on electronic delocalization and interactions between metal ions that reflect the system's stoichiometry, chemical nature, and the degree of mixed valency.<sup>6</sup> The present report shows that certain transition-metal hexacyanoferrate powders can act, depending on the oxidation state, as redox-conducting solid electrolytes or semiconducting or dielectric type materials.



**Figure 1.** Solid-state voltammetry of dry nickel hexacyanoferrate powders sandwiched between two glassy carbon slides: (A) the oxidized material containing 10% (by weight) of the reduced form; (B) the mixed-valent form containing hexacyanoferrates(III,II); (C) the fully oxidized and reduced materials. Scan rate was 50 mV s<sup>-1</sup>.

The current–potential curves, from solid-state electrochemical experiments, are demonstrated here for two types of metal substituted Prussian Blue analogues, nickel(II) hexacyanoferrate(III,II)<sup>1b,7</sup> and indium(III) hexacyanoferrate(III,II).<sup>2b</sup> These systems, when investigated as films on electrodes in the presence of a supporting electrolyte, are characterized by redox transitions originating only from the electron transfer in the ferri-/ferrocyanide portions of the materials. It is apparent from stoichiometric formulas (KNi<sup>II</sup>Fe<sup>III</sup>(CN)<sub>6</sub>, In<sup>III</sup>Fe<sup>III</sup>(CN)<sub>6</sub> and K<sub>2</sub>Ni<sup>II</sup>Fe<sup>II</sup>(CN)<sub>6</sub>, KIn<sup>III</sup>Fe<sup>II</sup>(CN)<sub>6</sub> for the oxidized and reduced forms, respectively) that the capacity of a mobile cation (K<sup>+</sup>), the so called “ion budget”,<sup>1d</sup> is much larger for nickel than indium hexacyanoferrates. The nickel analogue's structure is planar sheetlike<sup>1</sup> and has been found open enough to permit the unimpeded flux of all alkali-metal cations during electrochemical experiments with the respective supporting electrolytes.<sup>1b,7</sup> On the other hand, cation flow is much more restricted in indium hexacyanoferrates, and the differences should be retained in solid-state electrochemistry.

The solid-state voltammetry experiments were executed with two inert glassy-carbon slide electrodes that had been mounted in a sandwich configuration<sup>8</sup> (spacing between electrodes, ca. 0.6 mm; effective geometric area, 0.3 cm<sup>2</sup>) and filled with 20 mg of the evenly distributed well-ground cyanometalate powder. The materials were prepared by precipitation via dropwise mixing of equivalent amounts of 0.01 M solutions: K<sub>3</sub>Fe(CN)<sub>6</sub> or K<sub>4</sub>Fe(CN)<sub>6</sub> with NiCl<sub>2</sub> or InCl<sub>3</sub>, each containing KCl at a 0.5 M level. The mixed nickel hexacyanoferrate(III,II) systems were prepared in an analogous manner but via simultaneous precipitation of ferri- and ferrocyanides (at the desired ratio) with Ni(II) in 0.5 M KCl. The precipitation was followed by careful rinsing with distilled water. The stoichiometric formulas were verified by elemental analysis; the systems were found to be hydrated and contained, on average, five to seven structural water molecules. To perform voltammetric measurements, the electrodes were connected to a conventional electrochemical analyzer operated in a two-electrode mode. Thus the experimental concept somewhat resembled classical amperometry with two polarizable electrodes.

When the KNi<sup>II</sup>Fe<sup>III</sup>(CN)<sub>6</sub> powder, containing 10% of the reduced K<sub>2</sub>Ni<sup>II</sup>Fe<sup>II</sup>(CN)<sub>6</sub> form, was sandwiched between two glassy-carbon slides and subjected to potential cycling, after 2–3 full scans a steady-state well-developed voltammetric pattern was obtained (Figure 1A). The applied potential biases forced both ions and electrons to flow in response. If the system had behaved

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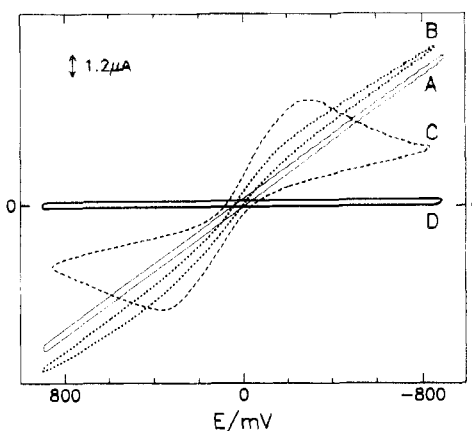
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simply as a semiconductor, the ohmic line would have been observed. Apparently, the system underwent redox transitions (Figure 1A) in which electron transfer must have been balanced by the flux of mobile potassium ions.

Introduction of some reduced sites into the oxidized material makes the system mixed valence, the equilibrium is established between hexacyanoferrates(III,II), and electron transfer is feasible. Indeed, the Figure 1A voltammetric pattern is characterized by a reversible redox transition around 0 V. Further, voltammetric peaks have been found proportional to the square root of scan rate (up to  $200 \text{ mV s}^{-1}$ ) showing that the overall process of charge propagation is diffusion controlled. It is noteworthy that the Figure 1A current-potential response does not reach a steady-state plateau form even at slow scan rates. The limiting current does not occur here, as was reported for certain mixed-valence polymer films studied with interdigitated array electrodes;<sup>1d,5c</sup> the thicknesses of the powders utilized here are relatively large, and diffusional rather than steady-state concentration gradients are established.

It can be hypothesized that the fully oxidized or fully reduced systems, containing no mixed-valence sites, would be nonelectroactive, at least in the Figure 1A potential limits. In order to synthesize such materials, highly pure potassium hexacyanoferrate components must be used, and the preparative steps must be done under an atmosphere of nitrogen. Indeed, the fully oxidized and reduced forms of nickel hexacyanoferrate powders,  $\text{K}_2\text{Ni}^{\text{II}}\text{Fe}^{\text{III}}(\text{CN})_6$  and  $\text{K}_2\text{Ni}^{\text{II}}\text{Fe}^{\text{II}}(\text{CN})_6$ , respectively, yield the overlapping responses characteristic of an insulator (Figure 1C). On the other hand, the system's truly mixed-valent form that contains the equivalent, and thus optimum, amounts of both ferri- and ferrocyanides started to show semiconducting-type behavior in the range of potentials  $\pm 0.5 \text{ V}$  (Figure 1B). The conductivity parameter, estimated from a slope of the resulting ohmic line as well as thickness and area of the sandwiched powder, was roughly  $10^{-5}$ – $10^{-4} \Omega^{-1} \text{ cm}^{-1}$ . This type of ohmic pattern may result from electronic delocalization in the 1:1 mixed-valent nickel hexacyanoferrate(III,II) material. Recently, evidence has been provided<sup>9</sup> that the dc conduction mechanism is predominantly sitewise electron hopping in truly dry Prussian Blue and its metal-substituted analogues, but any uptake of water or admixing with ionic material promotes ionic conductivity in the systems. Apparently, potassium is transported in the hydrated form, and the existing barriers to the movement of the ions are sensitive to moisture.<sup>1d</sup> It seems plausible to hypothesize that, in our 1:1 nickel hexacyanoferrate(III,II) system, which contains ca. five structural waters, mobility of potassium is not a dominating factor and contribution from electronic conductivity becomes important as well. Exposure of the powder to an atmosphere saturated with water vapors at  $50^\circ \text{C}$  for 5 min produces a system of high potassium mobility, and the resulting voltammetric currents are well defined and ca. an order of magnitude higher. On the other hand, dehydration of the powder by drying at  $90^\circ \text{C}$  for 5 min leads to ohmic behavior within the Figure 1 potential limits. In the case of our initial pentahydrate powder, which seems to be a mixed conductor with comparable contributions of electrons and ions, at more extreme potentials (exceeding  $\pm 1.0 \text{ V}$ ), the applied potential differences are large enough to cause the significant separation of charge and lead to redox effects. Consequently, the Figure 1B current-potential responses started to resemble voltammetric peaks. Their shapes are drawn out, but the currents were found to be dependent on potential scan rate; a linear relationship vs square root of scan rate was obtained but with a large positive intercept. The latter factor may originate from the ohmic type contribution. Note that the slope of the linear portion (in the  $\pm 0.5 \text{ V}$  range, Figure 1B) was not dependent on the scan rate at all.

Somewhat different current-potential responses were found for indium hexacyanoferrates (Figure 2) that contain less structural  $\text{K}^+$  than the nickel analogue. When the system's fully oxidized and reduced forms were placed in the sandwich, the semicon-



**Figure 2.** Current-voltage responses for indium hexacyanoferrate powders, sandwiched and subjected to potential cycling at  $50 \text{ mV s}^{-1}$ : (A) fully oxidized  $\text{In}^{\text{III}}\text{Fe}^{\text{III}}(\text{CN})_6$  form; (B) material formed upon addition of  $\text{KIn}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6$  to  $\text{In}^{\text{III}}\text{Fe}^{\text{III}}(\text{CN})_6$  (ratio of 0.25:1.0, by weight); (C) material formed upon further addition of  $\text{KIn}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6$  to  $\text{In}^{\text{III}}\text{Fe}^{\text{III}}(\text{CN})_6$  to yield a 0.5:1.0 ratio; (D) fully reduced  $\text{KIn}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6$  form.

ducting and dielectric patterns were obtained, respectively (curves A and D). It cannot be ruled out that the semiconducting response of the oxidized material,  $\text{In}^{\text{III}}\text{Fe}^{\text{III}}(\text{CN})_6$  (Figure 2A), originated from profound electronic interactions between the metal ions in this potassium-free structure. This was not a case for the potassium-containing reduced material,  $\text{KIn}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6$ , which behaved as an insulator and did not show any redox activity in the  $\pm 0.9 \text{ V}$  range of potentials. Application of more excessive potentials results in novel electroactivity patterns, but this will be a subject of a separate report.

Indium(III) hexacyanoferrate(III,II) modified electrodes, when exposed to  $\text{KCl}$  or  $\text{KNO}_3$  aqueous electrolytes, have been reported to exhibit reversible fast redox transitions.<sup>2b</sup> The difficulty in observing any redox conduction in the solid state (Figure 2A,D) is related to the lack of the mixed-valence redox sites in the system and, perhaps to some extent, the limited ionic budget of mobile potassium ions. To observe the Figure 1A type redox transitions, both ferri- and ferrocyanide portions must be present in sizable amounts in the powder. Indeed, addition (followed by mixing and grinding) of  $\text{KIn}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6$  to  $\text{In}^{\text{III}}\text{Fe}^{\text{III}}(\text{CN})_6$  in the ratio 0.25:1.0 (by weight) resulted in the appearance of some kind of peaks (Figure 2B) superimposed on the ohmic line characteristic of the  $\text{In}^{\text{III}}\text{Fe}^{\text{III}}(\text{CN})_6$  semiconducting behavior. When the amount of the reduced form in the mixed powder was increased to give the 0.5:1.0 ratio, the system showed a set of well-developed voltammetric peaks (Figure 2C) symmetrical around the point of 0 V. The above observations are consistent with the potential-driven electron transfer between indium hexacyanoferrates(III,II) that are in equilibrium. The shape of the indium hexacyanoferrate voltammetric peaks (Figure 2B,C) is more irreversible than in the case of a nickel analogue (Figure 1A), apparently as a consequence of the lower population, and perhaps mobility, of potassium ions that are necessary to provide balance during redox transitions. Nevertheless, the redox conduction process in Figure 2C is predominant, and no significant contribution from electrical conductivity is seen.

In conclusion, the scope of electrochemistry can be extended to studying solid-state redox transitions in mixed-valence ionically conducting inorganic powders. In fact, the systems can behave as mixed conductors, and the actual responses are dependent on the system's chemical identity, oxidation state, and stoichiometry. Our additional preliminary experiments suggest that, instead of powders, thin cyanometalate films can be utilized in solid-state voltammetry as well.<sup>10</sup>

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**Registry No.** C, 7440-44-0;  $\text{KNi}[\text{Fe}(\text{CN})_6]$ , 53295-14-0;  $\text{K}_2\text{Ni}[\text{Fe}(\text{CN})_6]$ , 13601-16-6;  $\text{In}[\text{Fe}(\text{CN})_6]$ , 15418-33-4;  $\text{KIn}[\text{Fe}(\text{CN})_6]$ , 55742-38-6;  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , 13746-66-2;  $\text{K}_4[\text{Fe}(\text{CN})_6]$ , 13943-58-3;  $\text{NiCl}_2$ , 7718-54-9;  $\text{InCl}_3$ , 10025-82-8;  $\text{KCl}$ , 7447-40-7;  $\text{K}$ , 7440-09-7.

(11) Present address: Department of Chemistry, University of Illinois, 1209 West California, Urbana, IL 61801.

Department of Chemistry  
University of Warsaw  
Pasteura 1, PL-02-093 Warszawa, Poland

Pawel J. Kulesza<sup>11</sup>

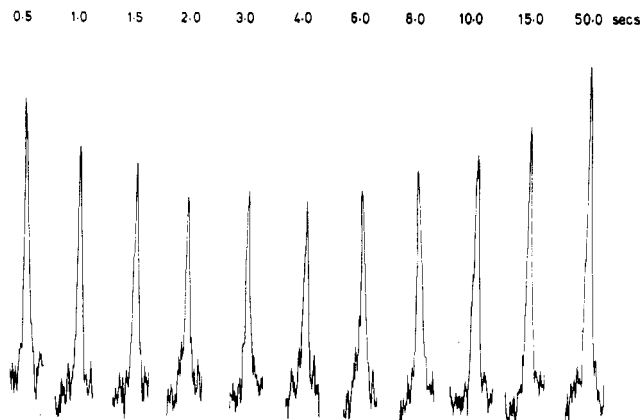
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### Nigericin-Mediated Transport of Cesium Ions through Phospholipid Bilayers Studied by a $^{133}\text{Cs}$ Magnetization-Transfer NMR Technique

The use of  $^7\text{Li}$ ,  $^{23}\text{Na}$ , and  $^{39}\text{K}$  NMR spectroscopy to study the transport of alkali-metal ions through the limiting membranes of cells<sup>1-6</sup> or through model phospholipid bilayers<sup>7-11</sup> is becoming an established technique. We now report that  $^{133}\text{Cs}$  NMR spectroscopy may be used to study the nigericin-mediated transport of  $\text{Cs}^+$  ions through phosphatidylcholine bilayers by use of a magnetization-transfer technique in a process shown to be first order in nigericin. The long relaxation time of the  $^{133}\text{Cs}$  nucleus allows extremely slow exchange rates (relative to those measurable by other dynamic NMR techniques) to be measured.

The NMR methods for the study of membrane transport of alkali-metal ions through model biological membranes that have been developed involve a compartmentalized system of cells (e.g. erythrocytes) or of vesicles and employ a shift reagent<sup>12</sup> or a relaxation agent<sup>13</sup> to contrast the signals from the intracompartamental and extracompartamental metal ions. For slow exchange rates the time course of signal intensities can be followed. For rapid exchange dynamic NMR line-broadening effects are observed. Magnetization transfer offers a third option for intermediate exchange rates that has so far not been fully utilized.<sup>11</sup>

The magnetization-transfer technique for a two-site case involves placing a magnetic label at one site by inverting the spin populations (inverted signal) and then following the signal intensity at the other site as the inverted signal relaxes back. If there is



**Figure 1.** Typical variation of the intensity of the  $\text{Cs}^+(\text{in})$  peak vs delay time ( $\tau$ ) for 25 mM  $\text{Cs}^+$  and nigericin. Conditions are as in Table I with rate  $k(\text{in} \rightarrow \text{out}) = 0.13 \text{ s}^{-1}$ . The reduction in signal intensity arises from transport of inverted magnetization from the  $\text{Cs}^+(\text{out})$  signal. The recovery arises from normal relaxation processes. The transport rate constant is obtained from the variation in signal intensity with time.

chemical exchange on the time scale of the relaxation process, a reduction in intensity of the monitored signal will be observed.<sup>11,14,15</sup>

The magnetization-transfer technique is most useful in the region where the transfer rates are similar to or somewhat slower than the relaxation rates, i.e. in the slow exchange limit just before measurable line broadening begins. We have previously used  $^7\text{Li}$  magnetization transfer to study the membrane transport of lithium mediated by the ionophores monensin<sup>9,11</sup> and M139603,<sup>10</sup> and it has also been used by Shungu and Briggs for  $^{23}\text{Na}$  transport studies.<sup>15</sup> We now report that a similar technique can be applied to  $^{133}\text{Cs}$  transport. To demonstrate this, we chose to examine transport mediated by nigericin, an ionophore known to favor the medium to large alkali-metal ions, whose maximum selectivity is for  $\text{K}^+$  and which should therefore transport  $\text{Cs}^+$  but with a much reduced efficiency.

$^{133}\text{Cs}$  NMR spectroscopy has been used by Davis, Murphy, and London to study the uptake of  $\text{Cs}^+$  ions into human erythrocytes and into perfused rat hearts.<sup>16</sup> These workers observed a chemical shift difference between the intra- and extracellular  $^{133}\text{Cs}^+$  resonances without the addition of shift reagent. In our vesicular systems there was no naturally occurring shift difference. It is, however, known that  $^{133}\text{Cs}$  chemical shifts are much more anion dependent than those of the other alkali metals, and we found that the resonance of  $^{133}\text{Cs}^+$  is shifted appreciably by the presence of linear triphosphosphate (PPPi) ions. The differences observed in cellular systems may well, therefore, arise from different anionic compositions between the intra- and extracellular fluids.

Vesicles were prepared by the dialytic detergent removal technique.<sup>7-11</sup> Typically egg yolk phosphatidylcholine (PC; 40  $\mu\text{mol}$ ) was dissolved in an aqueous 25 mM  $\text{CsCl}$  solution (2.0 mL) containing *n*-octyl glucopyranoside (ca. 600  $\mu\text{mol}$ ). Three dialyses against aqueous  $\text{CsCl}$  produced a suspension of large detergent-free unilamellar vesicles with the same concentration of  $\text{Cs}^+$  inside and out. The internal volume was ca. 11.5% of the total volume. A final dialysis was performed against aqueous  $\text{Cs}_3\text{PPPi}$  ( $[\text{Cs}^+]$  equimolar to earlier solution) with the ionic balance made up by choline chloride. This medium itself generated a chemical shift difference between the "in" and "out"  $^{133}\text{Cs}$  peaks by moving the out signal to higher frequency. No paramagnetic lanthanide was added as in previously reported experiments with other alkali metals.

The pulse sequence  $90^\circ - \tau_1 - 90^\circ - \tau - 90^\circ - \text{FID}$  was then employed with the transmitter set  $d$  Hz to low frequency of the  $\text{Cs}^+(\text{in})$  signal

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