Self-Assembled Films of Prussian Blue and Analogues: Structure and Morphology, Elemental Composition, Film Growth, and Nanosieving of Ions

Wanqin Jin,[†] Ali Toutianoush,[†] Mario Pyrasch,[†] Judit Schnepf,[†] Helmut Gottschalk,[‡] Werner Rammensee,[§] and Bernd Tieke^{*,†}

Institut für Physikalische Chemie der Universität zu Köln, Luxemburger Strasse 116, D-50939 Köln, Germany, II. Physikalisches Institut der Universität zu Köln, Zülpicher Strasse 77, D-50937 Köln, Germany, and Institut für Mineralogie und Geochemie der Universität zu Köln, Zülpicher Strasse 49b, D-50674 Köln, Germany

Received: April 9, 2003; In Final Form: September 3, 2003

Structure, morphology, and elemental composition as well as the size-selectivity of the ion transport behavior of ultrathin membranes of iron(III) hexacyanoferrate(II) (Fe^{III}HCF^{II}), iron(II) hexacyanoferrate(III) (Fe^{II}HCF^{III}), cobalt(II) hexacyanoferrate(III) (Co^{II}HCF^{III}), and nickel(II) hexacyanoferrate(III) (Ni^{II}HCF^{III}) are described. The membranes were prepared upon multiple sequential adsorption of metal cations and hexacyanometalate anions on porous polymer supports. Scanning electron and scanning force microscopy indicate that the membranes of the complex salts consist of a multitude of small, densely packed particles with diameter in the 10-100 nm range. Energy-dispersive X-ray analysis indicates that the iron hexacyanoferrate (Prussian blue) membranes consist of the potassium-rich, so-called "soluble" modification, KFe[Fe(CN)₆], while the membranes of the analogous complex salts consist of a mixture of the potassium-rich and potassium-free modification. The porous, zeolitic structure of the inorganic complex salts was permeable for ions with a small Stokes radius such as Cs⁺, K⁺, and Cl⁻, whereas large hydrated ions such as Na⁺, Li⁺, Mg²⁺, or SO₄²⁻ were blocked. Ion separation became progressively more effective, if the number of complex layers increased. The highest separation factors α (CsCl/NaCl) and α (KCl/NaCl) of 7.7 and 5.9, respectively, were found for the Fe^{III}HCF^{II} membrane subjected to a hundred dipping cycles. Membranes of iron(II), cobalt(II), and nickel-(II) hexacyanoferrate(III) were also useful for ion separation, but the α values were lower. Effects on the ion flux rates caused by the feed concentration and the polyelectrolyte precoating of the support are also discussed.

1. Introduction

The formation of ultrathin organized films with precise control over molecular arrangement and thickness in the nanometer range has been an active research area for several years.¹⁻⁵ Especially suited for film formation are methods of layer-bylayer assembly such as the Langmuir-Blodgett (LB) technique1-3 and methods of multiple sequential adsorption and chemisorption of organic compounds.^{4,5} Although most of the recent studies were concerned with polymeric films and organicinorganic hybrid films,⁶⁻⁸ the preparation of purely inorganic films has been described only very recently. Films of Prussian blue (PB),^{9–11} Ruthenium purple,¹⁰ or analogous mixed valence complex salts^{11,12} have been prepared upon multiple sequential adsorption (MSA) of transition metal ions and complex cyanometalate ions. The films are of practical interest for their electro- and photoresponsive properties,⁹ their ion exchange,^{13,14} and their ion separation behavior.11

PB and related metal hexacyanoferrate salts are known to exhibit an open, zeolite-like structure^{15–18} consisting of a cubic framework of iron centers bound by cyanide bridges such that additional cations can intercalate into the interstitial sites and indefinite amounts of water can be included. Because of the small channels in the lattice with a diameter of about 0.32 nm,

small hydrated ions such as Cs⁺ can penetrate the structure, whereas larger hydrated ions such as Na⁺ are blocked. Several studies were concerned with selective ion transport across thin films of PB and its analogues to an underlying electrode using a potential gradient as the driving force.¹⁹⁻²³ However, studies of ion transport across supported PB films, the transport being driven by a concentration gradient across the membrane, are very rare. A possible reason is that conventional PB films prepared upon electrochemical deposition,²⁴⁻²⁶ casting, or dipcoating from colloidal solution^{27,28} are not suited for this purpose. Electrochemical deposition does not allow films to be prepared on porous, nonconducting supports such as polymers, for example, and casting or dip-coating from colloidal solution do not provide a precise control of the thickness and lead to films with rather heterogeneous structure. The MSA technique overcomes these problems and allows for the preparation of dense, defect-free films on various supports. [Because metal hexacyanoferrate salts are known to organize in a cubic crystal lattice structure, a normal layering of metal cations and hexacyanoferrate anions is highly unlikely. Therefore, we avoid the term "layer-by-layer" deposition and instead use "multiple sequential adsorption".]

In a recent, comprehensive article,¹¹ we reported on the optical and electrochemical properties of films of PB and analogous complex salts, and for the first time, we demonstrated the application as being useful as ion sieving membranes. In an extension of the previous work, we here report on the structure and morphology of MSA films of PB and analogous complex

^{*} To whom correspondence should be addressed. E-mail: Tieke@uni-koeln.de.

[†] Institut für Physikalische Chemie der Universität zu Köln.

[‡] II. Physikalisches Institut der Universität zu Köln.

[§] Institut für Mineralogie und Geochemie der Universität zu Köln.

salts using scanning electron (SEM) and scanning force microscopy (SFM), the elemental composition using energydispersive X-ray spectroscopy (EDS), and the kinetics of the film growth using UV spectroscopy and SFM studies. Moreover, we present a detailed study on the use of the films as ion separation membranes. It is clearly demonstrated that the films represent nanosieves able to separate cesium, potassium, and ammonium ions from sodium, lithium, and magnesium ions, or chloride from sulfate ions.

2. Experimental Section

Materials. All chemicals were of analytical grade and used without further purification. $K_3[Fe(CN)_6] \cdot 3H_2O$, $K_4[Fe(CN)_6] \cdot$ 3H₂O, NiCl₂•6H₂O, NaCl, LiCl, NH₄Cl, and Na₂SO₄ were purchased from Fluka; CoCl₂•6H₂O, (NH₄)₂Fe(SO₄)₂•6H₂O, MgCl₂, and CsCl were purchased from Merck; FeCl₃, KCl, and polyvinyl sulfate potassium salt (PVS; molecular weight 350.000) were purchased from Acros; poly(diallyldimethylammonium chloride) (PDADMA; molecular weight 250.000) was purchased from Aldrich; and polyvinylamine (PVA; molecular weight 100.000) was kindly supplied by BASF, Ludwigshafen. Milli-Q-water (18 M Ω) was used for all experiments. A porous PAN/ PET membrane (Sulzer Chemtech GmbH, Neunkirchen) consisting of a polyethylene terephthalate (PET) fleece (thickness $100 \,\mu\text{m}$) coated with a polyacrylonitrile (PAN) layer (thickness 80 μ m) was used as the support, the pore size being 20–200 nm. For UV spectroscopic studies, quartz supports (Suprasil, $30 \times 12 \times 1$ mm³, Hellma GmbH, Müllheim/Baden) were used. The substrates were pretreated with PDADMA as previously described.11

Pretreatment of PAN/PET Supports. To render the substrate surface hydrophilic and negatively charged, it was treated with oxygen plasma. In a subsequent precoating step, the plasma treated support was dipped into a 0.01 molar aqueous PVA solution (pH 1.7) containing 1 M NaCl, in addition, so that a monolayer of the polyelectrolyte was adsorbed on the surface. Alternatively, the support was precoated with 3.5 layer pairs of PVA and PVS in alternating sequence,²⁹ the uppermost layer being PVA. The polyelectrolyte concentration of both solutions was 0.01 monomoles L^{-1} (monomoles = moles of monomer units), with the solutions containing 1 M NaCl as supporting electrolyte. For deposition, the plasma-treated substrate was first dipped into the PVA solution followed by rinsing with water and dipping into the PVS solution, etc. The dipping time was always 30 min. After pretreatment, the support had a positively charged surface layer of PVA.

Preparation of Prussian Blue, Cobalt, and Nickel Hexacyanoferrate Membranes. For the preparation of iron(III) hexacyanoferrate(II) (Fe^{III}HCF^{II}) membranes, aqueous solutions of 0.01 M K₄[Fe(CN)₆] + 0.1 M KCl (solution 1) and 0.01 M $FeCl_3 + 0.1 M KCl$ (solution 2) were used. A pretreated support was consecutively dipped into solution 1, pure water, solution 2, and pure water again. The four steps are denoted as a dipping cycle. They led to adsorption of a single Fe^{III}HCF^{II} layer. To obtain multilayer separating membranes, the four steps were carried out 20, 60, and 100 times, respectively. The dipping time into solutions 1 and 2 was 20 s each, the washing time in pure water was 1 min. The iron(II) hexacyanoferrate(III) (Fe^{II}-HCF^{III}) membrane was prepared according to the procedure for the $Fe^{III}HCF^{II}$ membrane except that aqueous solutions containing K₃[Fe(CN)₆] + 0.1 M KCl and 0.01 M (NH₄)₂Fe(SO₄)₂ + 0.1 M KCl were used. The cobalt(II) hexacyanoferrate(III) (CoII-HCF^{III}) and nickel(II) hexacyanoferrate(III) (Ni^{II}HCF^{III}) membranes were prepared accordingly except that aqueous solutions

containing 0.01 M K₃[Fe(CN)₆] + 0.1 M KCl and 0.01 M CoCl₂ + 0.1 M KCl, or 0.01 M K₃[Fe(CN)₆] + 0.1 M KCl and 0.01 M NiCl₂ + 0.1 M KCl, respectively, were used. The dipping time into the salt solutions was 5 min each, and the washing time in pure water was 10 min.

SEM Studies. The surface structure of the membranes was investigated using SEM (Philips SEM 515). The elemental composition of the surface was examined using EDS coupled to the SEM. EDAX DX-4 equipment was used. The accelerating voltage was 15 keV to stimulate X-ray emission. Characteristic X-rays with an energy between 0 and 10 keV were collected using a Si detector with a Be window. This permitted identification of elements with atom number $Z \ge 7$. Each spectrum was acquired for 10 min over a 400 × 300 μ m² region. After background subtraction, the peaks were fit to a Gaussian function using a least-squares routine to calculate intensities.

SFM Studies. SFM images were taken with a Nanoscope IV SFM (Digital Instruments) working in contact mode. The samples were investigated in air at room temperature. The images were taken in equiforce mode, and commercially available Si/N cantilevers with integrated tips were used.

UV/Visible Spectroscopy. UV/visible absorption spectra were recorded using a Perkin-Elmer Lambda 14 spectrometer. The absorbance was corrected by subtracting the signal of the pure quartz substrate.

Ion Permeation Measurements. Measurements of ion permeation were carried out using a homemade apparatus which has been described elsewhere.^{11,30} The membrane (area A =4.52 cm²) was mounted between two chambers with a volume V_0 of 60 mL each. Chamber one contained the electrolyte solution of concentration c = 0.1 mol/L, and chamber two contained pure water and the cell for measurement of the conductivity Λ . The flux rate J of electrolytes across the membrane was determined by measuring the initial increase of conductivity $\Delta \Lambda$ per unit time Δt under constant stirring. J was calculated from the equation $J = (\Delta \Lambda / \Delta t)(V_0 - \Delta V)\Lambda_m^{-1} A^{-1}$ with Λ_m being the molar conductivity of the corresponding salt solution and $(V_0 - \Delta V)$ being the volume in chamber two after correction of the osmotic flow. The change of the J value upon the correction was never larger than 2%. The separation factor α is defined as the ratio of the flux values of the corresponding salts.

3. Results and Discussion

3.1. Morphology of Self-Assembled Films of Prussian Blue and Analogues. The ultrathin membranes of the metal hexacyanoferrate salts were prepared according to the MSA-technique described in previous articles^{9,11} and briefly outlined in the experimental part. Because we were interested in membranes displaying a size-selective flow of ions through the zeolitic channels of the crystal lattice of the complex salts, it was crucial to prepare dense, defect-free films not showing any nonselective transport through defects and voids. Preliminary SFM studies¹¹ indicated that the desired films can be obtained at the easiest, if at least 20, better 60 dipping cycles are applied. In Figure 1, the typical appearance of $7 \times 5 \text{ cm}^2$ sections of various metal hexacyanoferrate membranes on PAN/PET supports is shown. All membranes were prepared upon 60 dipping cycles. The Fe^{III}-HCFII and FeIIHCFIII membranes exhibit the typical blue color of PB, and the Co^{II}HCF^{III} and Ni^{II}HCF^{III} membranes are pink and yellow, respectively. All membranes exhibit a very homogeneous coloration. In Figure 2, scanning electron micrographs of the surface structure of metal hexacyanoferrate membranes prepared upon 60 dipping cycles are shown. The surface



Co^{II}HCF^{III}

Ni^{II}HCF^{III}

Figure 1. Macroscopic appearance of various metal hexacyanoferrate membranes on PAN/PET support prepared upon 60 dipping cycles. Size of membrane sections: 7×5 cm².

structure of all of the samples is very similar, independent from the nature of the deposited transition metal cations. The surface consists of numerous small particles of different sizes adsorbed on a smooth support with an undulating height profile as recognizable from the bright and dark parts of the background in Figure 2a. At higher magnification, it can be seen that the surface consists of many small particles with diameters between 10 and 100 nm and some large particles with a diameter up to 0.3 micrometers (Figure 2b). The Ni^{II}HCF^{III} membrane appears slightly more homogeneous than the cobalt-containing membrane, because the particles are generally smaller and more uniform in size (Figure 2b,c). The Fe^{II}HCF^{III} sample shown in Figure 2, parts d and e, also consists of many small and a few large particles, which are equally distributed over the whole surface. An even more detailed view can be obtained from the SFM pictures shown in Figure 3. In Figure 3a, the undulating structure of the support is clearly visible. Many small particles adsorbed on the surface can be recognized, which represent the adsorbed layer of Fe^{III}HCF^{II}. At higher magnification, the small particles with diameter less than 0.1 μ m and maximum height of about 50 nm are clearly resolved (Figure 3b,c). Again the particles of the nickel-containing film (Figure 3b) appear smaller and more uniform than the particles of the cobalt-containing film (Figure 3c). In general, the morphology of all sequentially adsorbed metal hexacyanoferrate films is similar. The particle size found in the self-assembled films is also similar to the crystallite size found in the bulk material precipitated from solution.31

3.2. Growth of Prussian Blue Films. To get a more detailed information on the membrane formation, we studied the growth of Fe^{II}HCF^{III} films as a function of the number of dipping cycles and the dipping time into each solution. The studies were carried out using UV/visible spectroscopy and SFM. For the UV studies, the Fe^{II}HCF^{III} films were built up on quartz substrates pretreated with a monolayer of PDADMA. The UV studies allow the amount of adsorbed PB to be determined from the absorbance of the charge-transfer band at 700 nm. In Figure 4, the absorbance of the PB films dipped for either 1, 5, or 15 min





Figure 2. Typical surface structures of various metal hexacyanoferrate membranes prepared upon 60 dipping cycles. Scanning electron micrographs of Co^{II}HCF^{III} (a,b), Ni^{II}HCF^{III} (c), and Fe^{II}HCF^{III} (d,e) membranes at different magnification.



Figure 3. Scanning force microscopic images of $Fe^{III}HCF^{II}$ (a), Ni^{II} -HCF^{III} (b), and $Co^{II}HCF^{III}$ (c) membranes at different magnification. Membranes were prepared with 60 dipping cycles. Support: porous PAN/PET membrane.

into the individual electrolyte solutions is plotted versus the



Figure 4. Plot of absorbance of Fe^{II}HCF^{III} films versus the number of dipping cycles. The dipping time into each solution was either 1, 5, or 15 min. Substrate: Quartz precoated with a single PDADMA layer.

number of dipping cycles. As expected, the absorbance increases nearly linearly with the number of dipping cycles, but to our surprise, the increase is highest for the sample dipped for only 1 min and lowest for the sample dipped for 15 min into each solution. After 20 dipping cycles, the sample with dip times of 15 min only exhibits about 40% of the absorbance of the shortly dipped sample, and the absorbance values scatter strongly. We ascribe this effect to a partial desorption of ions or even complete detachment of PB particles from the surface during the prolonged immersion. To scrutinize our assumption, we studied the morphology of samples dipped into each solution for either 30 or 1 min using SFM. As shown in Figure 5a, only a few isolated particles with 50-100 nm in diameter and less than 20 nm in height are deposited on the surface, if the dipping time was 30 min and the sample was subjected to 5 dipping cycles. When the number of dipping cycles is increased, more and more particles are deposited, and particle aggregates are also formed. Some of the particles shown in Figure 5b exhibit the typical cubic shape of PB crystallites. However, even after 10 dipping cycles, the bare substrate surface is still visible in some places. After 20 cycles, the whole surface is coated with particles, with the size and height being very different (Figure 5c). Substrates dipped into each solution for only 1 min exhibit a complete surface coverage with particles after 5 dipping cycles already (Figure 5d) and with an increasing number of dipping cycles, the thickness of the PB film increases (Figure 5e). From the study, it can be concluded that dense, homogeneous membranes of the metal hexacyanoferrate salts can only be prepared if the dipping times of the substrates are kept very short.

3.3. Elemental Composition. Metal hexacyanoferrates are known to exist in a so-called "soluble", potassium-rich, form and an insoluble, potassium-free, modification. In the case of PB, the soluble form has the composition $KFe^{III}[Fe^{II}(CN)_6]$, whereas the relevant compositions of soluble cobalt- and nickel hexacyanoferrate are $KCo^{II}[Fe^{III}(CN)_6]$ and $KNi^{II}[Fe^{III}(CN)_6]$, respectively. The stoichiometric formulas of the potassium-free salts are $Fe^{III}_4[Fe^{II}(CN)_6]_3$, $Co^{II}_3[Fe^{III}(CN)_6]_2$, and $Ni^{II}_3[Fe^{III}(CN)_6]_2$. It may be added that the term "soluble" only refers to the colloidal solubility and not to an ionic solubility of the complex salt. To find out which of the possible forms is adsorbed on the substrate, the elemental composition of the films was determined using EDS measurements. Typical EDS diagrams of $Fe^{III}HCF^{II}$ and $Co^{II}HCF^{III}$ membranes are shown in Figure 6. Although the $Fe^{III}HCF^{II}$ membrane exhibits two strong



Figure 5. Scanning force microscopic images of $Fe^{II}HCF^{III}$ films as a function of dipping cycles and dipping time into each solution. Dipping times are 1 min (a,b) and 30 min (c-e). Numbers of dipping cycles are 5 (a,c), 10 (b,d), and 20 (e).

 K_{α} peaks for Fe (6.402 keV) and K (3.311keV) (Figure 6a), the cobalt- and nickel-containing membranes show three K_{α} peaks originating from Co (6.97 keV), Fe and K (Figure 6b), or Ni (7.204 keV), Fe and K, respectively (not shown). The quantitative evaluation of the peak areas allows an estimation of the molar composition at the surface of the membranes. In Table 1, the molar ratios of the elements are listed (except for C and N, which were not determined). Because of the relatively inhomogeneous surface structure, the absolute values may be affected with an error up to 10%. However, it can be recognized that the PB-based membranes nearly exclusively consist of the soluble, potassium-containing modification. In the case of the cobalt- and nickel-containing membranes, the analysis is more difficult. The high potassium content indicates that the potas-



Figure 6. Typical EDS diagrams of X-ray intensity vs energy for Fe^{III}-HCF^{II} (a) and Co^{II}HCF^{III} (b) membranes subjected to 60 dipping cycles.

TABLE 1: EDS Analysis of Fe^{III}HCF^{II}, Co^{II}HCF^{III}, and Ni^{II}HCF^{III} Membranes (60 Dipping Cycles; PAN/PET Support Pretreated with One Layer PVA)

	molar ratio of elements						
separating membrane	experimental		theoretical	stoichiometric formula			
Fe ^{III} HCF ^{II}		Fe:K					
	$1:0.42^{a}$		1:0.5	KFe ^{III} [Fe ^{II} (CN) ₆]			
			1:0	Fe ₄ ^{III} [Fe ^{II} (CN) ₆] ₃			
Co ^{II} HCF ^{III}		Co:Fe:K					
	1:0.70:0.43		1:0.67:0	$\text{Co}_3^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]_2$			
			1:1:1	KCo ^{II} [Fe ^{III} (CN) ₆]			
Ni ^{ll} HCF ^{III}		Ni:Fe:K					
	1:0.74:0.43		1:0.67:0 1:1:1	Ni ₃ ^{II} [Fe ^{III} (CN) ₆] ₂ KNi ^{II} [Fe ^{III} (CN) ₆]			

^{*a*} Chloride found (Fe:K:Cl = 1:0.42:0.03).

sium-rich, "soluble" modification is present in excess. However, the cobalt and nickel content are significally higher than the potassium and iron content. This indicates that certain amounts of the potassium-free modifications are also present; that is, the cobalt-and nickel-containing membranes actually represent mixtures of both modifications. A recent study of the cyclo-



Figure 7. Plot of flux rates of various electrolyte salts across Fe^{III} -HCF^{II} membranes (100 dipping cycles) vs the Stokes radius r_h of the hydrated cations.

voltammetric response of the self-assembled films came to the same conclusion. $^{11}\,$

3.4. Nanosieving of Ions. Our studies of the ion transport were mainly aimed at demonstrating the ion sieving effect, i.e., the exclusive transport of those ions across the membrane, whose diameter is smaller than the zeolitic pore size of the metal hexacyanoferrate separating membrane.

As the first step, a separating membrane of PB was prepared by 100-fold alternate dipping of the porous support into aqueous solutions of ferric chloride and potassium hexacyanoferrate-(II). The large number of dipping cycles was chosen in order to make sure that the ion transport is dominated by the flow through the zeolitic pores of the complex salt and that the flow through voids and defects is supressed. The next step was to determine the flux rates of various electrolyte salts across the membranes. For this purpose, the increase in conductivity per unit time, $\Delta\Lambda/\Delta t$, was measured in the permeate chamber. Further details on the measurement and calculation of the flux rate are given in the experimental part. As the electrolytes, we used alkali metal chlorides, ammonium and magnesium chloride, and sodium sulfate.

In Figure 7, the flux rates of the electrolyte salts are plotted versus the ion radii $r_{\rm h}$ of the hydrated cations³² also denoted as Stokes radii. Only chloride salts were investigated because the chloride ion exhibits a Stokes radius of only 0.121 nm. This value is significantly smaller than the radius of the zeolitic pores of the separating membrane of 0.16 nm, and thus, the anions should be smoothly able to pass the membrane. As can be derived from Figure 7, the electrolyte salts with cation radii smaller than the pore size of the membrane such as cesium, potassium, and ammonium chloride exhibit high flux rates of about $9-12 \times 10^{-10}$ mol cm⁻² s⁻¹. In contrast, sodium, lithium, and magnesium chloride, with Stokes radii of the cations larger than the zeolitic pores, exhibit low flux rates of $0.2-1.5 \times 10^{-10}$ mol $cm^{-2} s^{-1}$; that is, they are largely rejected. The fact that some of these ions are still able to pass the membrane can be ascribed to a timely, partial dehydration of these ions, which requires only little energy and is accompanied by a shrinking of the radius to values below the Stokes radius. High selectivities α (Cs⁺/Na⁺) and α (K⁺/Na⁺) of 7.7 and 5.9 were found, in good agreement with the previously published preliminary data.¹¹.

3.4.1. Effect of the Number of Dipping Cycles on the Ion Flux. We also studied the ion flux of Fe^{III}HCF^{II} membranes subjected to less dipping cycles. As indicated in Table 2, the flux increases and the selectivity decreases, if the number of dipping cycles

TABLE 2: Flux Rates and Selectivities of Various Electrolyte Salts (c = 0.1 M) through Fe^{III}HCF^{II} Membranes with Different Numbers of Dipping Cycles^{*a*}

	flux rate $[10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}]^*$					selectivity ^b		
dipping cycles	CsCl	NH ₄ Cl	KC1	NaCl	LiCl	MgCl ₂	α (CsCl/NaCl)	α (KCl/NaCl)
20	23.0	19.0	18.9	15.7	13.8	8.8	1.5	1.2
60	16.9	15.0	14.0	4.1	2.1	1.3	4.1	3.4
100	11.7	10.0	8.9	1.5	1.1	0.2	7.7	5.9

^{*a*} Support: PAN/PET precoated with a single PVA layer. ^{*b*} Experimental error: \pm 5 to 10%.

TABLE 3: Flux Rates and Selectivities of Various Electrolyte Salts (c = 0.1 M) through Metal Hexacyanoferrate Membranes with 60 Dipping Cycles and a Different Polyelectrolyte Precoating of the Porous PAN/PET Support

	flux rate $[10^{-10} \text{ mol cm}^{-2} \text{ s}^{-1}]^*$				selectivity ^a			
membrane	CsCl	KCl	NaCl	LiCl	MgCl ₂	Na_2SO_4	α (CsCl/NaCl)	α (KCl/NaCl)
(a) Precoating: Single Layer PVA								
Co ^{II} HCF ^{III}	50.4	41.7	29.1	30.3	26.6	26.3	1.7	1.4
Ni ^{II} HCF ^{III}	46.3	42.1	33.7	30.4	24.2	23.3	1.4	1.2
Fe ^{II} HCF ^{III}	32.1	29.9	11.1	7.8	2.3	1.6	2.9	2.7
(b) Precoating: Layer Sequence (PVA/PVS) ₃ -PVA								
no	20.2	21.5	12.9	7.8	2.2	3.8	1.6	1.7
Co ^{II} HCF ^{III}	9.6	7.5	3.9	4.5	1.2	0.9	2.5	1.9
Ni ^{II} HCF ^{III}	9.3	7.4	5.5	3.3	0.2	0.1	1.7	1.2

^{*a*} Experimental error: \pm 5 to 10%.

is reduced to 60 or even 20. The sample subjected to 60 dipping cycles still exhibits a significant ion sieving effect: The flux rates of electrolyte salts with cations of a Stokes radius below the zeolitic pore size of 0.16 nm are significantly higher than for salts with a hydrated cation radius above 0.16 nm. However, the lower selectivities of $\alpha(Cs^+/Na^+)$ of 4.1 and $\alpha(K^+/Na^+)$ of 3.4 indicate an additional flux through voids and defects although the transport through the zeolitic pores is still dominating. If only 20 dipping cycles are applied, the flux rate is even higher, and the corresponding selectivities are merely 1.24 and 1.2. For this membrane, the transport through defects is obviously so large that the sieving effect is no longer significant.

3.4.2. Ion Flux across Membranes of Fe^{II}HCF^{III} and Analogues. The ion transport across Fe^{II}HCF^{III}, Co^{II}HCF^{III}, and Ni^{II}-HCF^{III} membranes was also investigated. The flux rates are represented in Table 3. All membranes were prepared upon 60 dipping cycles, and the porous PAN/PET membrane was used as the substrate. To improve the adsorption of the inorganic ions, the support was either precoated with a single PVA layer or a sequence of PVA/PVS bilayers, with the layer sequence being (PVA/PVS)₃-PVA. We first discuss the ion flux across the membranes with a single PVA layer. From Table 3a, it is recognizable that the flux rates of cesium and potassium chloride are always higher than those of the other electrolyte salts sodium, lithium, and magnesium chloride and sodium sulfate. Further, it is noticed that the Co^{II}HCF^{III} and Ni^{II}HCF^{III} membranes show nearly identical flux rates. Compared with the two membranes, the Fe^{II}HCF^{III} membrane exhibits approximately 25% lower flux rates for cesium and potassium chloride, and about 70-90% lower rates for the other salts. However, the flux rates of the Fe^{II}HCF^{III} membrane are two to three times higher than those of the Fe^{III}HCF^{II} membrane, which by far shows the lowest flux rates and the highest selectivities. For the cobalt- and nickelcontaining membranes, the selectivity α (CsCl/NaCl) is 1.7 and 1.4, respectively, whereas for the Fe^{II}HCF^{III} and Fe^{III}HCF^{II} membranes, it is 2.9 and 4.1.

Because the size of the zeolitic channels is largely equal for all complex salts, the different transport behavior can only be ascribed to the different thickness and morphology of the individual membranes. Although the thickness of the separating membranes was not measured directly, it was possible to estimate the thickness ratio of the Fe^{III}HCF^{II} and Fe^{II}HCF^{III} films from the absorbance of their charge-transfer bands at 700 nm. At equal number of dipping cycles, the absorbance of the Fe^{III}-HCF^{II} films was always about 30% higher than for the Fe^{II}-HCF^{III} films. This means that 30% more complex salt was adsorbed and that the thickness should thus be about 30% higher as well. The reason for the difference is that the Fe^{III}HCF^{II} films are built up from cations and anions of larger charge numbers $z^+ = 3$ and $z^- = 4$ than the Fe^{II}HCF^{III} films, which only consist of ions with $z^+ = 2$ and $z^- = 3$. Thus, the charge density on the substrate is lower, and consequently, less ions are adsorbed per dipping cycle. Because the flux across the membrane is inversely proportional to the thickness, it can be concluded that Fe^{II}HCF^{III} membranes exhibit flux rates which are 1.4 times higher than those for the Fe^{III}HCF^{II} membranes. The lower thickness will go along with a higher number of defects and voids, which again should lead to higher flux rates. In fact, this is in agreement with the experimental observations.

The Ni^{II}HCF^{III} and Co^{II}HCF^{III} membranes are also built up from ions of low charge density, which partly explains their high flux rates. In addition, it must be taken into account that two crystalline forms are present as is known from the EDS measurements and the cyclovoltammetric studies.¹¹ The simultaneous presence of the two forms is the reason that individual crystallites are smaller and the defect concentration in the membrane is higher. This again increases the ion flux and may explain the high flux rates observed for these membranes.

3.4.3. Ion Flux across Membranes Precoated with Polyelectrolyte Multilayers. To improve the selectivity of the metal hexacyanoferrate membranes, the thickness of the polyelectrolyte precoating of the porous polymer support was increased. Instead of adsorbing a single PVA layer, the layer sequence (PVA/PVS)₃-PVA was built up by alternately dipping the PAN/ PET support into aqueous solutions of PVA and PVS. It was hoped that the thicker precoating provides a higher charge density on the support so that the metal hexacyanoferrate membrane is more homogeneously and densely adsorbed. As indicated in Table 3b, the substrate plus thicker polyelectrolyte precoating and no complex salt adsorbed exhibits lower flux rates than all complex salt membranes with a single PVA layer as a precoating displayed in Table 3a. The precoating with 3.5



Figure 8. Effect of concentration in the aqueous KCl feed solution on the flux rate across Co^{II}HCF^{III}, Ni^{II}HCF^{III}, and Fe^{III}HCF^{II} membranes (60 dipping cycles) on PAN/PET support precoated with a single PVA layer.

polyelectrolyte bilayers causes some selectivity in ion transport, with the α (CsCl/NaCl) value being 1.6, for example. Previous studies on ion transport across polyelectrolyte multilayer membranes have shown that the permeation rates of various alkali metal chlorides are inversely proportional to the charge density of the cations because of their different electrostatic repulsion by the positively charged polyelectrolytes in the membrane. If cobalt and nickel hexacyanoferrate are adsorbed on the supports with a thick polyelectrolyte precoating, the flux rates are further decreased and the selectivity α (CsCl/NaCl) is increased to 2.5. Although the separation behavior can be improved in this way, the excellent quality of the Fe^{III}HCF^{II} membranes is not achieved.

3.4.4. Effect of Feed Concentration on Ion Flux. To study the effect of the electrolyte concentration c on the ion flux rate J, we investigated several aqueous KCl feed solutions in the concentration range from 1 millimol/L to 2 mol/L. It can be seen from the log-log-plot in Figure 8 that J increases nearly linearly with c over at least 4 orders of magnitude, the relationship being $J = 3.48 \times 10^{-8} c^{0.98}$ (J in mol cm⁻² s⁻¹ and c in mol L⁻¹) for Co^{II}HCF^{III}, and $J = 4.38 \times 10^{-8} c^{0.98}$ for Ni^{II}HCF^{III}. For Fe^{III}HCF^{II}, the relation was $J = 1.56 \times 10^{-8}$ $c^{1.24}$. The almost identical transport behavior of the cobalt and nickel hexacyanoferrate membranes can be ascribed to their similar morphologies. The linearity of the relation between Jand c indicates that the ions do not interact electrostatically with the membrane material, so that the flux is simply a function of the concentration gradient across the membrane as it is expected for ion sieving.

4. Conclusions

In our study, the growth, structure, elemental composition, and ion transport behavior of ultrathin, self-assembled films of mixed valent metal hexacyanoferrate salts are described. The kinetic studies of the film formation indicate a two-step growth process while the substrate is dipped into the dipping solutions. The first step comprises the rapid adsorption of counterions at the surface, whereas in the second, much slower step, controlled crystal growth sets in comprising ion desorption and readsorption under formation of 3D crystallites. To prepare homogeneous films, it is therefore necessary to dip the substrate only shortly, i.e., less than a minute into each of the dipping solutions. This is clearly very different from the adsorption behavior of polyionic organic compounds, which have a much lower tendency to crystallize.

The studies of structure and elemental composition indicate that the PB membranes consist of the potassium-rich, soluble form of the complex salts, KFe[Fe(CN)₆], whereas the Co^{II}-HCF^{III} and Ni^{II}HCF^{III} membranes consist of a mixture of the potassium-containing and potassium-free forms. The complex salts are present as small crystallites of less than a hundred nanometers in diameter. With increasing number of dipping cycles, the crystallites more and more form a dense, homogeneous film on the substrate.

The ion transport studies show that especially the Fe^{III}HCF^{II} membranes prepared upon 60 or more dipping cycles are dense enough to act as ion filters able to separate small hydrated ions from large ones, for example Cs⁺ or K⁺ from Na⁺. Maximum selectivities of a(CsCl/NaCl) of 7.7 and a(KCl/NaCl) of 5.9 are found. The values are clearly superior to those of crownether-containing polymer membranes,^{33,34} which are about 1.5-2.5, or polyelectrolyte multilayer membranes, which are about 1.5.^{35,36} The high selectivities in Cs/Na ion transport suggest applications of the Fe^{III}HCF^{II} membranes in the separation of radioactive cesium from other nontoxic salts in nuclear waste solutions, for example. That the transport is based on a nanosieving mechanism is first indicated by the fact that only ions with a Stokes radius smaller than the zeolitic pore size of the crystal lattice of PB can pass the membrane and second by the rather low selectivity α (NaCl/MgCl₂) = 3.1 indicating that electrostatic effects originating from a different charge density of the cations only play a minor role.

Acknowledgment. The authors are grateful to Dr. A. Hübner, Sulzer Chemtech, Neunkirchen, for kindly providing the plasma-treated PAN/PET-supporting membranes. The Deutsche Forschungsgemeinschaft is thanked for financial support (projects Ti 219/6-2 and 7-1). One of us (W.J.) thanks the Alexander von Humboldt foundation for a scholarship.

References and Notes

(1) Roberts, G. G. Langmuir Blodgett Films; Plenum Press: New York, 1990.

(2) Ulman, A. Ultrathin Organic Films; Academic Press: Boston, 1991.

(3) Tredgold, R. H. Order in thin organic films; Cambridge University Press: New York, 1994.

(4) Handbook of polyelectrolytes and their applications; Tripathy, S. K., Kumar, J., Nalwa, H. S., Eds.; American Scientific Publishers: Stevenson Ranch, 2002, Vol. 1.

(5) *Multilayer Thin Films*; Decher, G., Schlenoff, J. B., Eds.; Wiley-VCH: Weinheim, Germany, 2003.

(6) Bertrand, P.; Jonas, A.; Laschewsky, A.; Legras, R. Macromol. Rapid Commun. 2000, 21, 319.

(7) Hammond, P. T. Curr. Opinion Colloid Interface Sci. 2000, 4, 430.

(8) Tsukruk, V. V. Prog. Polym. Sci. 1997, 22, 247.

- (9) Pyrasch, M.; Tieke, B. Langmuir 2001, 17, 7706.
- (10) Millward, R. C.; Madden, C. E.; Sutherland, I.; Mortimer, R. J.;

Fletcher, S.; Marken, F. Chem. Commun. 2001, 1994.

(11) Pyrasch, M.; Toutianoush, A.; Jin, W.; Schnepf, J.; Tieke, B. Chem. Mater. 15, 245.

(12) Barathi, S.; Nogami, M.; Ikeda, S. Langmuir 2001, 17, 7468.

(13) Jeerage, K. M.; Schwartz, D. T. Sep. Sci. Technol. 2000, 35, 2375.

(14) Lin, Y.; Fryxell, G. E.; Wu, H.; Engelhard, M. Environ. Sci. Technol. 2001, 35, 3962.

(15) Keggin, J. F.; Miles, F. D. Nature 1936, 137, 577.

(16) Haya, K.; Uchida, I.; Neff, V. D. Acc. Chem. Res. 1986, 19, 162.

(17) Buser, H. J.; Schwarzenbach, D.; Petter, W.; Ludi, A. Inorg. Chem. 1977, 16, 2704.

(18) Herren, F.; Fisher, P.; Ludi, A.; Halg, W. Inorg. Chem. 1980, 19, 956.

(19) Koncki, R. Crit. Rev. Anal. Chem. 2002, 32, 79.

(20) Karyakin, A. A. Electroanalysis 2001, 13, 813.

(21) Schneemeyer, L. F.; Spengler, S. E.; Murpy, D. W. Inorg. Chem. 1985, 24, 3044.

(22) Haya, K.; Shoji, N.; Uchida, I. J. Am. Chem. Soc. 1984, 106, 3423.
 (23) Shankaran, D. R.; Narayanan, S. S.; Fresenius, J. Anal. Chem. 1999, 365, 663.

- (24) Itaya, K.; Ataka, T.; Toshima, S. J. Am. Chem. Soc. 1982, 104, 4767.
 - (25) Lundgren, C. A.; Murray, R. W. Inorg. Chem. 1988, 27, 933.
 - (26) Neff, V. D. J. Electrochem. Soc. 1985, 132, 1382.
 - (27) Toshima, N.; Liu, K.; Kaneko, M. Chem. Lett. 1990, 485.
 - (2) Posimia, P., Ed. R., Falos, M. Orem. Ed. 19
 (28) Neff, V. D. J. Electrochem. Soc. 1978, 125, 886.
 (29) Decher, G. Science 1997, 277, 1232.
- (30) Tieke, B.; Ackern, F. v.; Krasemann, L.; Toutianoush, A. Eur. Phys. J. E 2001, 5, 29.
- (31) Ludi, A. Chem. Unserer Zeit 1988, 22, 123.

(32) Pau, P. C. F.; Berg, J. O.; McMillan, W. G. J. Phys. Chem. 1990, 94, 2671.

(33) Beginn, U.; Zipp, G.; Möller, M. Adv. Mater. 2000, 12, 510.

(34) Thunhorst, K. L.; Noble, R. D.; Bowman, C. N. J. Membr. Sci. **1999**, *156*, 293.

(35) Toutianoush, A.; Tieke, B. Mater. Sci. Eng. C 2002, 22, 459.

(36) Toutianoush, A.; Tieke, B. In Novel Methods to Study Interfacial Layers; Möbius, D., Miller, R., Eds.; Elsevier Science: Amsterdam, 2001; p 415.