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Georges Grevillot · Julia Dzyazko
Konstantin Kazdobin · Vladimir Belyakov

The electrochemically controlled sorption of *d*-metal cations by ion exchangers based on titanium phosphate

Abstract A study of the sorption of *d*-metal ions by titanium phosphate on a platinum electrode shows that the potential of the platinum electrode significantly influences the uptake of cations by the ion-exchanger. Cathodic polarization leads to a significant increase of the sorption whereas anodic polarization is accompanied by desorption. Therefore it is possible to perform cycles of sorption and desorption simply by switching the potential. The results obtained can be explained by the fact that the layer of titanium phosphate acts as a phase which extracts protons or hydroxide ions. The electrochemical generation of hydroxide ions at negative potentials can, especially at less acidic pH, lead to the formation of metal hydroxides in the ion-exchanger phase. This interference is less important at a lower solution pH.

Key words Ion · Uptake · Inorganic ion-exchanger · Proton conductor

Introduction

As a rule, all ion-exchange materials (IEM), which are able to exchange their protons with other cations from a solution, are solid proton conductors, in which the charge carriers are labile protons of acid functional groups. The high proton conductivity of such ion-exchangers as hydrated zirconium phosphate, polyantimonic acid, and membranes of the Nafion and

Flemion types [1–3] allows use of these materials as solid electrolytes in various electrochemical devices.

The simple model of proton transport in the system consisting of the Pt electrode-solid proton conductor (ion-exchanger)-electrolyte was proposed previously [4]. In this case, under polarization a difference arises between the activities of the protons on the electrode and on the outer part of the attached IEM granule. The transfer process probably consists of adsorption of protons from water on the ion-exchanger particle-solution interface (this interface includes not only the external but also the internal surface of particles, i.e. pores) and their transport through the bed of the ion-exchanger to the current collector, where electrochemical reactions occur (Fig. 1a). The role of the ion-exchanger is reduced to the translation of the near-electrode layer to the outer surface of the granule.

According to this concept, possible replacement of labile protons by metal cations leads to their introduction into the ion-exchanger. This will certainly provoke an increase of the sorption capacity of the system (Fig. 1b). Upon changing the sign of polarizing potential, the reverse process will occur. The protons generated on the current collector will migrate through the ion-exchanger bed and replace the sorbed cations.

The penetration depth of an electrode process into the ion-exchanger bed is determined by the ratio of the proton conductivity of the ion-exchanger to the conductivity of the solution; the bulk of the ion-exchanger will behave similar to a three-dimensional electrode only when the conductivity of the IEM exceeds that of the solution [4]. Therefore, the main criterion for the choice of materials for an electrochemically controlled uptake is a high proton conductivity.

The materials based on the phosphates of elements of group 4 (especially their amorphous modifications) satisfy this requirement [1]. Their proton conductivity is considerable and reaches 10^{-4} S cm^{-1}. Moreover, these materials are characterized by a high sorption capacity and selectivity, and considerable stability with regard to

G. Grevillot
Laboratorie des Sciences du Genie Chimique, CNRS-ENSIC, 1 rue de Grandville, F-54001, Nancy, France

J. Dzyazko · K. Kazdobin · V. Belyakov (✉)
Vernadskii Institute of General & Inorganic Chemistry
Ukrainian National Academy of Sciences
32/34 Palladin Avenue, 252680 Kiev – 142, Ukraine
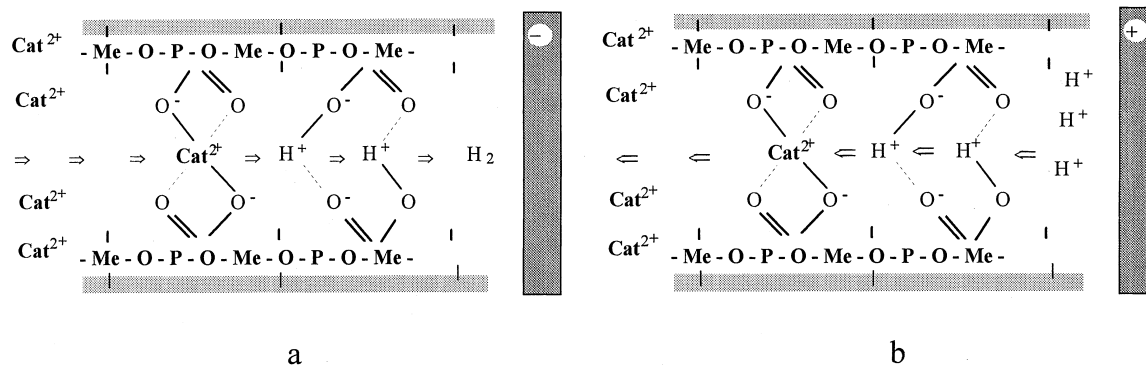e-mail: v-bel@mail.kar.net, Tel./Fax: +380-44-4443212

a   b

Fig. 1 Models of proton (**a**) and cation (**b**) transfer in a polarized ion-exchanger [4]

the effect of aggressive agents, electromagnetic fields and high-level radiation [5, 6].

Thus, the proton conductivity of inorganic phosphate ion-exchangers allows the possibility of electrochemically controlled sorption processes on these materials. In connection with this phenomenon it was necessary to study the influence of polarization on the uptake of non-ferrous metal ions by phosphate-containing ion-exchangers.

Experimental

The samples of titanium phosphate (TiPh) chosen for investigation were synthesized in the manner similar to the approach described by Strelko [7], with the following characteristics: molar ratio P:Ti = 0.78; granule diameter 0.5–0.8 mm; specific surface 200 m^2 g^{-1}; moisture content 60%.

The effect of TiPh polarization was deduced from studies of the uptake of the cations Cu^{2+}, Co^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+} from chloride solutions. NaCl (0.05 M) was used as background electrolyte, and 0.001 M NaCl as eluent.

The uptake and electrochemical studies were carried out with the ratio of ion-exchanger (g)/solution (ml) equal to 1:100. The content of sorbed components in 0.001 M solutions was measured by UV-vis spectrophotometry [8] with a PYE Unicam PU 8800 and by atomic adsorption with a PYE Unicam SP-9-800. The Cu^{2+} dithiocarbamate complex, Co^{2+} thiocyanate complex and Zn^{2+} and Cd^{2+} dithisone complexes were used for spectrophotometric determinations. The values of the sorption capacity were calculated from the obtained data in a manner similar Markhol [9].

When solutions with higher concentration were used, the determination of the cation-exchange capacity was carried out using a procedure analogous to that of Lascorin et al. [10]. The ion-exchanger samples had been removed from the cell and dried at room temperature for 48 h. Then a weighed portion of 0.1 g had been put into 10 ml of a 10% solution of sulfuric acid. The amount of eluted cations was determined by atomic absorption.

The electrochemical measurements were carried out in a cylindrical cell used for studies of three-dimensional electrode systems [4, 11]. The experimental arrangement is described elsewhere [12]. A single layer of ion-exchanger granules was placed onto the Pt-mesh current collector at the bottom of the cell. The potential of the current collector was measured versus a Ag/AgCl reference electrode by means of a Luggin capillary placed close to the current collector surface. The Pt counter-electrode was placed behind the porous diaphragm in the upper part of the cell. Polarization was achieved in the potentiostatic mode by using a fPI-50–1 potentiostat (ZIP Instruments, Russia). No metal deposition was observed

on the current collector upon polarization. All potential values are reported versus the standard hydrogen electrode. All experiments were carried out at a temperature of 20 ± 2 °C.

Results and discussion

The results of the influence of the polarization of TiPh on the uptake of Co^{2+} ions from 0.001 M solutions at various pH values are shown in Fig. 2a. The analysis of these data allows us to conclude that cathodic polarization results in an increase of the sorption capacity of the ion-exchanger. When the polarizing potential is shifted to cathodic values, the sorption activity of the material increases. An increase of the concentration of the sorbate or addition of background electrolyte leads to a diminishing of the uptake of the cations (Fig. 2b).

A maximum increase in sorption occurs at $E = -0.3$ V. At more negative values of the polarizing potential the studies of the sorption properties of TiPh were not conducted because, owing to its hydrolysis, deterioration of the mechanical properties and of the sorption characteristics of the ion-exchanger takes place.

Studies of the uptake of other *d*-metal cations under conditions of the maximum uptake of Co^{2+} ions (pH 5, $E = -0.3$ V) have shown (Table 1) that in all cases the cathodic polarization of IEM leads to a significant increase of sorption.

During preliminary experiments it has been shown that the concentration of sorbate, at which the uptake rate both on polarized and on non-polarized TiPh does not depend on the amounts of the components, is 0.01 M and above. After interruption and subsequent continuation of the process, the uptake of non-ferrous metal ions again increases. Further, it was found that an increase of the dispersity of the material results in an increase of the uptake rate. The latter did not depend on the intensity of the circulation of the working solution. This may confirm that the rate determining step of the sorption is the diffusion into the bulk of the ion-exchanger particle [13].

It may be considered that in the case of classical ion exchange the kinetics of diffusion within the particles is observable only when the concentration of the exchanging ions is not less than 0.1 M [14]. In our case, this limiting concentration is decreased due to complex
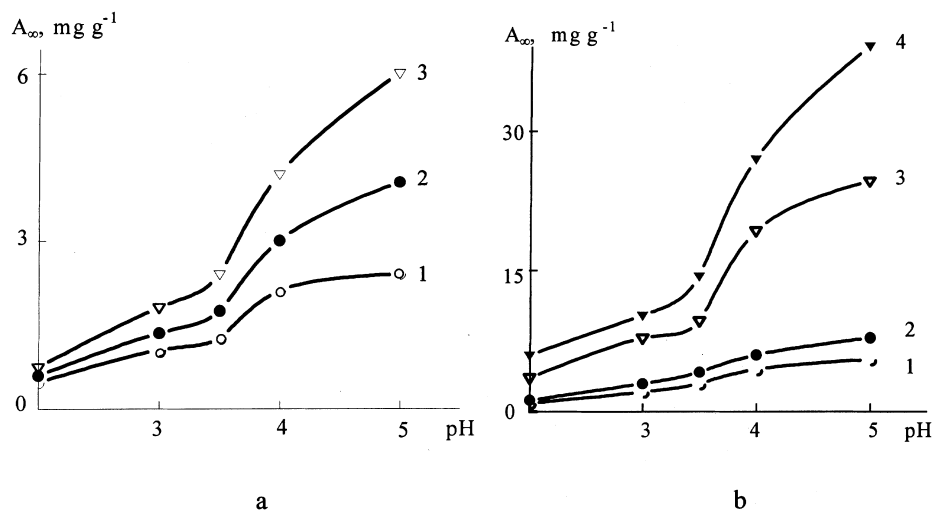
Fig. 2a, b Dependence on pH of Co^{2+} ion uptake on polarized and non-polarized IEM. **a** Electrolyte = 0.001 M $CoCl_2$ (*1*); non-polarized; $E = -0.1$ V (*2*); -0.3 V (*3*). **b** Electrolyte = 0.05 M NaCl + 0.001 M $CoCl_2$ (*1, 2*); 0.01 M $CoCl_2$ (*3, 4*); *1, 3*: non-polarized; *2, 4*: E = -0.3 V

formation in the ion-exchanger phase [15]. Such a process is characteristic for TiPh [16].

To analyze the experimental data of solutions containing 0.01 M of a component, the mathematical apparatus of the Boyd-Adamson theory [14] was applied. According to this theory, the rate of ion exchange is described by the following equation:

$$F = 1 - \frac{6}{\pi^2} \sum_{n-1}^{\infty} \frac{1}{n^2} e^{-n^2 Bt} \qquad (1)$$

where $F = A_+/A_\alpha$ is degree of process completion; A_+ is the quantity of an adsorbed component at a certain time; A_α is the quantity of an adsorbed component at equilibrium, determined after 48 h of contact; and n is an integer number, $1 < n < \infty$. The value of the apparent diffusion coefficient, D_i (calculated from the seven A_+-t data points) is related to the B value from Eq. 1 as follows:

$$B = \frac{\pi^2 D_i}{r^2} \qquad (2)$$

where r is the radius of a particle (in our case r was 9×10^{-2} cm). The values Bt for all F values are calculated in Reichenberg [17].

The order of ion uptake is basically opposite to that of the pH at which the hydroxide formation of the sorbed ions occurs: the lower the critical pH, the higher the uptake. So TiPh shows the highest sorption capacity for Cu^{2+} ions which precipitate at low pH as hydroxide. Ni^{2+} ions, which precipitate as hydroxide at high pH values, exhibit only a small influence of polarization on sorption. As can be seen from Table 1, the polarization results in an increase of the apparent diffusion coefficient (D_i) of the d-metal cations in the TiPh phase. The comparison of diffusion coefficients with the values of sorption capacities shows that the sequence of cation mobilities is opposite to the order of sorption affinities to TiPh.

The results obtained are in accordance with the theory of bond formation and breaking of ions in the sorbent phase [18]. According to this theory, an increase of the diffusion rate of the sorbed components into the grains of the polarized sorbent can be explained in terms of a decrease of the difference between the time of binding ions to the functional groups of the sorbent and the time for their migration from one group to another, when compared with a non-polarized ion-exchanger.

Table 1 Uptake capacity A_∞ and effective factors of diffusion D of d-metal ions at sorption on TiPh at cathodic polarization ($E = -0.3$ V) and without it at pH 5

Cation	Uptake from 0.001 M Solution			Uptake from 0.01 M solution				Characterization of changes		
	A_∞, Non-polarized TiPh (mg g^{-1})	A_∞, Polarized TiPh (mg g^{-1})	Increase in A_∞, (%)	Polarized TiPh		Non-polarized TiPh		Increase in A_∞, (%)	Increase in D_i (%)	pH of hydroxide formation [19]
				D_i (10^9 cm^2 s^{-1})	A_∞ (mg g^{-1})	D_i (10^9 cm^2 s^{-1})	A_∞ (mg g^{-1})			
Cu^{2+}	3.49	13.02	272	1.24	63.54	0.71	21.60	194	75	4.2
Zn^{2+}	1.95	5.20	167	1.83	20.26	0.81	11.43	77	125	5.4
Co^{2+}	2.36	5.90	150	1.94	33.04	1.04	20.94	57	86	6.6
Ni^{2+}	0.58	1.17	100	2.40	10.27	1.20	7.33	40	100	6.7
Cd^{2+}	1.99	4.63	133	2.22	33.76	1.13	17.87	89	96	7.2

The order of increasing D_i values coincides with the sequence of pH for hydroxide formation.

The data obtained allow us to expect efficient extraction of easily hydrolyzed cations with polarized TiPh from rather dilute mixed solutions. The results of ion uptake from a mixture are shown in Fig. 3. They are described in terms of

$$W = C_t/C_0 \times 100\% \qquad (3)$$

where W is the degree of ion removal; C_t is the concentration of ions in time t; and C_0 is the initial concentration.

A cathodic polarization promotes an increase of uptake, first of all, for cations with the lowest pH for hydroxide formation. Consequently, Cu^{2+} ions (curve 4) are extracted at first and almost completely from the solution, whereas Ni^{2+} ions, needing a higher pH for hydroxide formation, are extracted mainly after Cu^{2+} ions (curve 2). So cathodic polarization permits the extraction of ions from mixed solutions (see also [20]).

An anodic polarization was expected and found to result in a desorption of previously adsorbed (by TiPh) cations (Fig. 4). Thus the degree of regeneration of the ion-exchanger R is determined by the value of the polarizing potential: the more anodic it becomes, the higher is the extent of desorption. The order of desorption is: $Ni^{2+} > Cd^{2+} > Co^{2+} > Zn^{2+} > Cu^{2+}$. The given order coincides with the apparent diffusion coefficient D_i of the corresponding ions. At the same time, it is opposite to the sequence of pH values at which hydroxide formation occurs and opposite to the sorption affinities of cations.

The possibility of a multiple use of TiPh for the sorption of non-ferrous metal cations from a solution was also studied. For this purpose, a number of cyclic sorption-desorption experiments of Co^{2+} cations on polarized TiPh were performed. The sorption was carried out from a solution containing 0.001 M of sorbed component in the presence of the background electrolyte. The results are presented in Table 2. It can be seen
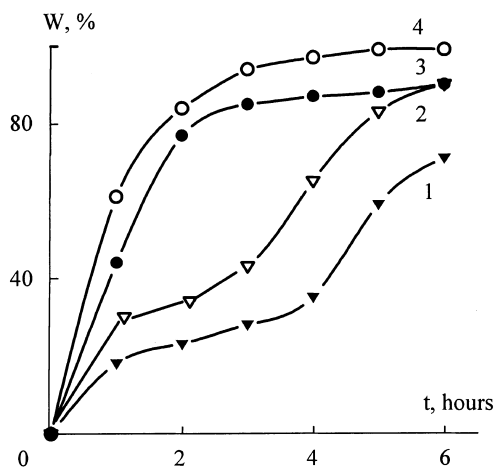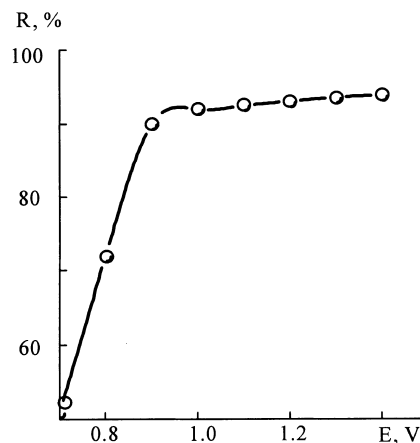

Fig. 4 Dependence of IEM regeneration rate, R saturated previously by Co^{2+} ions, on applied anodic potential value. Eluent: 0.001 M NaCl; pH 5.9

that, during 10 cycles, the uptake efficiency practically did not change, though some increase of ion-exchanger residual capacity from cycle to cycle was observed. No noticeable deterioration of mechanical or uptake characteristics of TiPh was found.

The results obtained can be explained by considering the bed of TiPh as a proton extracting (or accepting) phase similar to that described previously [4]. In fact, under cathodic polarization the proton transport in the system (current collector)-TiPh-solution results in reducing the concentration of hydrogen ions in the solution layer directly adjacent to the surface of the ion-exchanger when compared to its concentration in the bulk of the solution. This occurs because of the decrease of the concentration of protons near the ion-exchanger, which cannot be compensated by migration.

The lack of concentration of H^+ ions near the electrode is the result of their transfer from the solution phase to the ion-exchanger phase. Thus, it is possible to assume that under cathodic polarization the generation of OH^- ions takes place directly on the ion-exchanger surface. This fact originates from the shift of an ion-exchange equilibrium (Eq. 4) towards the formation of the cation-substituted form of TiPh. If the concentration of H^+ ions in the solution is small (pH > 3), the pH in the near-to-electrode layer will greatly exceed the pH of the bulk of the solution [21].
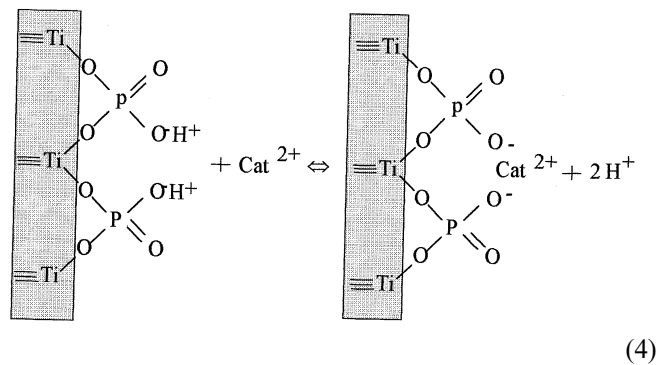

Fig. 3 Uptake of Cu^{2+} and Ni^{2+} ions from multicomponent solutions (W degree of component uptake). Solution composition (mg l^{-1}): [Ni^{2+}], 29 (1, 2); [Cu^{2+}], 32 (3, 4); ph 6. 1, 3: non-polarized; 2, 4: under polarization of −0.3 V

$$(4)$$

Table 2 Change of uptake capacities A_∞ of TiPh during the cyclic process of sorption-desorption for Co^{2+} ions (uptake at $E = -0.3$ V, pH 5, desorption at $E = 1.2$ V, pH 5.5)

No. of cycle	Sorption (0.001 M $CoCl_2$ + 0.01 M NaCl or 0.13 g $l^{-1}CoCl_2$)		Desorption (0.001 M NaCl)	
	Residual contents of Co^{2+} (mg l^{-1})	A_∞ (total) (mg g^{-1})	Degree of regeneration, R, %	A_∞(residual) (mg g^{-1})
1	<1	4.72	90	0.47
2	<1	5.19	87	0.65
3	<1	5.31	84	0.85
4	<1	5.36	84	0.88
5	<1	5.60	79	1.18
6	<1	5.90	75	1.47
7	<1	6.19	70	1.86
8	<1	6.58	63	2.42
9	<1	7.14	48	3.69
10	1.50	8.35	43	4.25
11	2.40	8.76	39	5.34
12	3.00	9.76	38	6.05

Therefore, the most pronounced increase of sorption capacity of the polarized ion-exchanger, in comparison to the non-polarized one, is observed in the pH range close to neutrality. The increase of solution concentration results in the reduction of the buffer capacity of the TiPh bed. Therefore, the influence of polarization on ion-exchanger sorption activity is higher in more dilute solutions.

Parallel to the intensification of the ion-exchange process of Eq. 4, basification can result in the formation of polymeric hydroxo complexes of non-ferrous metal ions in the ion-exchanger phase. The detected relation between sorption of ions and the pH of their hydroxide formation supports the possibility of this process. Besides, in the phase of the polarized ion-exchanger, in comparison to the non-polarized system, the apparent diffusion coefficient D_i reaches greater values for cations having higher pH values for the formation of hydroxides. It may be concluded that the influence of polarization on the intradiffusion mobility of ions is related to the intensifying of hydrolysis in the sorbent phase [22] under cathodic polarization. The most probable explanation of electrochemical desorption concerns the local acidification of ion-exchanger at anodic polarization. This causes a shift of the equilibrium of Eq. 4 to the left, on the one hand, and the dissolution of hydroxo complexes, precipitated in the ion-exchanger phase during sorption, on the other.

Conclusions

It can be concluded that the sorption of *d*-metal ions by TiPh can be controlled by external polarization. This fact allows a considerable increase in the efficiency of uptake, and also allows multiple applications of the sorbent.

The authors consider the influence of polarization on local pH changes inside the ion-exchanger to be very important. Indeed, hydrogen and oxygen evolution occurs under large overvoltage even on the Pt electrode. The process was studied under conditions of small currents, which flow through the electrochemical cell at various potentials, preceding the electrode process. So the formation of H^+ or OH^- occurs in the bulk of the ion-exchanger, but no visible hydrogen or oxygen evolution occurs on the current feeder.

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