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Cr(VI) transport through ceramic ion-exchange membranes for treatment of industrial wastewaters

YU. S. DZYAZKO[1,*], A. MAHMOUD[2], F. LAPICQUE[2] and V.N. BELYAKOV[1]
[1]*V.I. Vernadskii Institute of General & Inorganic Chemistry, Palladin Ave., 32/34, 03142, Kiev, Ukraine*
[2]*Laboratoire des Sciences du Génie Chimique, CNRS-ENSIC, 1 rue Grandville, F-54042, Nancy, France*
*(*author for correspondence, e-mail: dzyazko@ionc.kar.net)*

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Abstract

This work is devoted to assessment of the possibility of using ceramic membranes, which contain an ion-exchange component, such as hydrated zirconium dioxide (HZD), for Cr(VI) removal from dilute solutions by electrodialysis. Transport properties of the membranes were investigated. HZD-containing membranes were found to be permeable to anions in acidic media while they demonstrate cation-exchange properties in alkaline media. Cr(VI) anion transport through HZD membranes was studied. It was shown that an increase in the amount of ion-exchanger in the membrane results in a rise in electrodialysis efficiency. The transport number of Cr(VI) species was found to range from 0.33 to 0.63 for currents below the limiting current. It was also shown that increasing the concentration of H^+ or Cr(VI) ions in the solution to be purified allows higher rate of Cr(VI) ion transport through the membrane.

List of symbols

a	activity (mol m^{-3})
A	area (m^2)
$C_{\mathrm{Cr,s}}$	concentration of Cr(VI) in the bulk of solution (mol m^{-3})
$C^0_{\mathrm{Cr,s}}$	concentration of Cr(VI) in the solution at themembrane surface (mol m^{-3})
$D_{\mathrm{Cr,s}}$	Cr(VI) diffusion coefficient in the solution (m^2 s^{-1})
d	distance between the membrane and cathode (m)
E	cell voltage (V)
E_{m}	membrane potential (V)
F	Faraday constant (96485 A s mol^{-1})
i	membrane current density calculated with allowance for the outersurface area (A m^{-2})
$i_{\mathrm{Cr,lim}}$	limiting membrane current density caused by transport of Cr(VI) ions (A m^{-2})
k_{Cr}	mass transport coefficient of Cr(VI) ions (m s^{-1})
L	membrane length (m)
$N_{\mathrm{Cr,m}}$	flux of Cr(VI) ions through the membrane (mol m^{-2} s^{-1})
$N_{\mathrm{Na,m}}$	flux of Na^+ ions through the membrane (mol m^{-2} s^{-1})
$n_{\mathrm{Cr,a}}$	amount of Cr(VI) ions in the anolyte (mol)
$n_{\mathrm{Na,c}}$	amount of Na^+ ions in the catholyte (mol)
R	gas constant (8.314 J mol^{-1} K^{-1})
T	temperature (K)
$t_{\mathrm{Cr,m}}$	transport number of Cr(VI) ions through the membrane (dimensionless)
$t_{\mathrm{Cr,s}}$	transport number of Cr(VI) ions through the solution (dimensionless)
u	superficial flow rate (for the cathode compartment) (m s^{-1})
z	charge of species (dimensionless)

Greeks

γ	ratio of anion over cation valences (dimensionless)
κ	specific conductivity (Ohm^{-1} m^{-1})
τ	time (s, h)
ν	kinematic viscosity (m^2 s^{-1})

Dimensionless Groups

Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number

1. Introduction

The electrodialytic technique can be considered as a promising method for the removal of Cr(VI) anions from dilute solutions.

Some of the features of chromium anion transport through anion-exchange membranes based on organic polymers have been studied [1, 2]. Unfortunately the membranes, which traditionally contain quaternary amino groups, degrade due to the high oxidative activity of Cr(VI), especially at high temperature [3]. Anion-exchange membranes obtained by plasma grafting of aminosiloxane groups on polyvinylidene fluoride support were developed by Roualdes et al. [3] for the removal of hexavalent chromium. Such membranes were found to be stable in oxidizing media; however the maximum transport number of Cr(VI) reached only 0.15.

Microporous ceramic diaphragms are known to be stable against oxidizing agents [4]. This allows their use for the electrodialytic removal of heavy metal cations from chromium plating solutions [5–8]. These materials permit both the solvent and the ions to be transferred due to their hydraulic permeability. In order to prevent a backward cation flux from the concentrate compartment of the electrodialysis cell to the desalination chamber, the electrodialysis process is usually associated with deposition of cations in the cathode compartment due to alkalization of the catholyte.

However, ceramic diaphragms act as both convection and diffusion barriers due to their relatively small pore size (0.1–50 μm) [9], though these separators are not selective. Nevertheless the conventional inorganic ceramic materials used as chlorine-alkali diaphragms, e.g. asbestos, exhibit noticeable ion exchange properties.

It was previously shown that microporous composite ceramic membranes, containing cation-exchange compounds e.g. hydrated zirconium dioxide (HZD), can be used for electrodialysis [10]. HZD is known to possess amphoteric properties [11]. Depending on the solution pH these materials demonstrate anion-exchange properties in acidic media:

$$\begin{aligned}&\mathrm{ZrO_m(OH)_{p-1}(OH_2)^+ + An^-}\\&\leftrightarrow \mathrm{ZrO_m(OH)_{p-1}(OH_2)^+An^-}\end{aligned} \tag{1}$$

or cation-exchange behaviour in alkaline media:

$$\mathrm{ZrO_m(OH)_{p-1}O^- + Cat^+ \leftrightarrow ZrO_m(OH)_{p-1}O^-Cat^+}. \tag{2}$$

Here Cat^+ and An^- are cation and anion respectively, *m* and *p* are integers. The ion-exchange properties of HZD strongly depend on pH in acidic media the anion-exchange capacity gradually increases with decreasing pH and reaches a constant value at pH < 2. At the same time, in alkaline media increasing the solution pH leads to an increase in cation-exchange capacity, which remains constant at rather high pH.

It should be expected that insertion of ion-exchange components into the inert ceramic matrix will improve the membrane materials due to enhancement of their selective properties. In this context, the aim of the work was to assess the possibility of using membranes, which contain *HZD*, for electrodialytic Cr(VI) removal from dilute solutions. It is the first attempt to use ceramic membranes as materials selective towards anions.

2. Experimental

2.1. *Membranes*

2.1.1. *Synthesis of membranes*

The inert ceramic matrix produced by *Inma* (Ukraine) consisted of Al_2O_3 (70 wt.%) and ZrO_2 (30 wt.%). The porosity of the matrix was 40%, the average pore diameter and specific surface were estimated as 190 nm and 5 $m^2\ g^{-1}$, respectively. The membranes were made in the form of tubes with an external diameter of 12 mm and 1 mm thick. The membranes were originally used as diaphragms to separate different sections of reactors for electrochemical processes.

The Ion-exchange component (*HZD*) was inserted into the inert matrix using the method developed as follows:

1. Preparation of $\mathrm{ZrO_m(OH)_p}$ sol by gradual addition of a 1 M NH_4OH solution to a 1 M $ZrOCl_2$ solution under thorough stirring. The solution volume ratio was approx. 1:1. The synthesis was performed at 330 K. The obtained sol was stored during 48 days at 298 K, before its use for membrane synthesis.
2. Impregnation of the membrane with the sol. The membrane was stored in the sol during 24 h and then washed with deionized water up to effluent pH 4–5.
3. Treatment of the membrane with a 1 M NH_4OH solution, washing with deionized water up neutral reaction of the effluent.
4. Drying of the membrane at 298 K up to constant weight.

This procedure was carried out once to prepare *HZD-1* membrane samples, four times for *HZD-2* materials, and 7 times for *HZD-3* materials.

2.1.2. *Investigation of ion-exchange properties*

The total anion-exchange capacity of the membranes was determined as follows. A weighted amount of sample (2–3 g) was immersed in 50 cm^3 of 0.1 M HCl for 24 h. Then the samples were washed with deionized water and treated with 50 cm^3 of 0.1 M NaOH. The Cl^- ion content in the recovered liquid was determined by potentiometric titration using $AgNO_3$ solution after acidification with 0.1 M HNO_3 [12].

Sorption of Na^+ ions was also investigated: the samples were immersed in 50 cm^3 of 1 M NaOH solution for 24 h, then washed with the same volume of 1 M HCl. The Na^+ content in the resulting solution was determined using a *PFM-U4.2* flame photometer.

2.1.3. *Measurement of membrane potential*

Before electrochemical experiments the membranes were treated with 0.1 M HCl and washed with deionized water up to neutral reaction of the effluent.

A tube membrane was sealed hermetically at its bottom and then placed vertically in a glass vessel containing a 0.01 M HCl solution. The membrane tube was filled with a 5×10^{-3} M HCl solution. Two Ag/AgCl electrodes were immersed in the solutions inside and outside the membrane. The membrane potential was measured using a *V*7-34A high-resistance voltmeter.

After the measurements, both the inner and the outer solutions were removed from the tube membrane and the vessel respectively. The concentration of each solution was determined by the potentiometric method.

2.1.4. *Measurements of electrical conductivity*

A cylindrical cell (inner diameter of 1.6 cm, length of 13 cm) made of stainless steel was used to measure the membrane conductivity. A 0.5 cm-rhodium rod was fixed inside the cell. The inner surface of the cylinder was coated with a rough platinum layer and acted as the cathode, while the rod was the anode. The membrane was inserted between the two cylindrical electrodes in the cell. The axes of the membrane, rod and cylinder coincided. Both the inner and the outer spaces of the cell were filled with the same 5×10^{-3} M or 1×10^{-4} M H_2SO_4 solution. Investigations of sorption of Cl^- (Na^+) ions and electrochemical properties of the membranes were carried out at 298 K using a *UTU-2/77* thermostated bath.

The resistance measurements were performed by impedance spectroscopy using a PGSTAT 30 (Autolab) system. The membrane resistance was calculated as the difference between the cell resistances with and without a membrane similarly to [13]. The cell constant of a particular device was determined without a membrane using a standard 0.1 M KCl solution.

The surface conductivity was defined as the ratio of the electrical conductivity of the membrane to its thickness [9].

2.1.5. *Investigation of porous structure*

Porosity and pore size distributions were investigated by means of mercury porosimetry using a *Promoter 2000* device. Before experiments the samples were dried at 435 K and stored in a desiccator over P_2O_5.

2.2. *Investigation of Cr(VI) transport*

2.2.1. *Experimental set-up*

The experimental set-up consisted of a cell, which was described in section 2.1.3., two separate liquid lines and measurement instrumentation (Figure 1). The electrolyte circuit connected to the anode compartment had a volume of 200 cm^3 (the anolyte vessel was divided to register the change of the liquid volume during the experiments). The liquid in this line was circulated by means of a peristaltic pump (*NP-1 M*) with a flow velocity of 1.5 cm^3 s^{-1}. The Cr(VI)-containing catholyte solution prepared from analytical grade $K_2Cr_2O_7$ was circulated at 0.93 cm^3 s^{-1} through the outer compartment in ''once-through'' mode using a second peristaltic pump (*Zalimp PP 2–15*).

A *B5-49* power supplier was used to maintain a constant current. The cell voltage and current were measured by means of a *V7-34/A* voltmeter and a *SCH-4311* multimeter respectively (the current density was calculated with allowance for the outer effective area of the membrane). The pH of the solution at the cathode compartment outlet was controlled with an *EV-74* pH meter. In some cases the anolyte pH was maintained at the predetermined level by addition of NaOH solution aliquots.

The solution circulated through the anode compartment as well as the inflow solution through the cathode compartment were thermostated at 298 K.

2.2.2. *Investigation of electrodialysis*

During the electrodialysis process the following system variables were monitored: the concentration of Cr(VI), Cr(III), H^+ (OH^-), Na^+, K^+ species in the anode compartment, the concentration of Cr(III) and H^+ at the cathode compartment outlet, cell voltage, as well as the volume of the anolyte and catholyte.

Samples were taken at regular intervals from the cathode and anode compartments and then analysed. The Cr(VI) concentration in the samples was determined by atomic absorption using a *PUY UNICAM SP 9* spectrometer. Determination of Cr (III) content was carried out using a *Shimadzu UV-Vis mini*

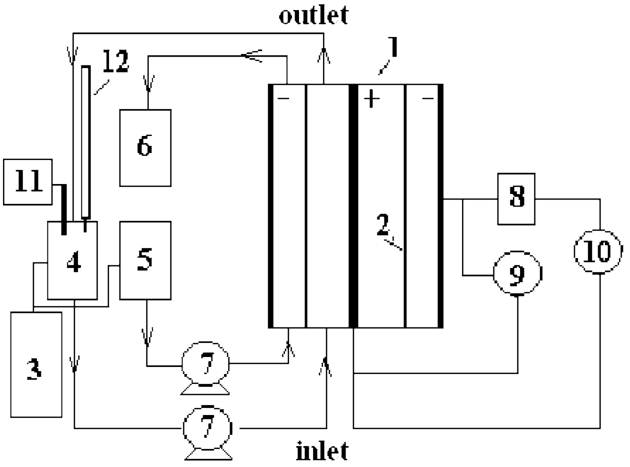

Fig. 1. Experimental set-up for investigation of ion transport: electrodialysis cell (1), membrane (2), thermostatic bath (3), anode reservoir (4), reservoir with initial Cr(VI) containing solution (5), waste reservoir (6), pumps (7), power supplier (8), voltmeter (9), ammeter (10), pH-meter (11), burette with NaOH solution (12).

1240 spectrophotometer in the wavelength range of 600–800 nm. The H^+ content of the solution was estimated by pH measurements. Na^+ and K^+ ion concentrations were determined by flame absorption photometry.

The rate of Cr(VI) transport to the anode compartment was estimated using anolyte analysis data. The rate of Na^+ transport to the cathode compartment was calculated from the decrease of Na^+ concentration in the anolyte.

After each experiment the membrane was removed from the cell and washed thoroughly with 2 M H_2SO_4 and deionized water until the disappearance of the yellow colour of the membrane.

3. Results

3.1. *Ion-exchange and electrochemical characteristics of membranes*

Characteristics of *HZD-1-HZD-3* membranes are shown in Table 1. It follows from the table that the membranes exhibit both anion-and cation-exchange properties. The total ion-exchange capacities for Na^+ and Cl^- ions are practically the same. Higher concentrations of *HZD* species in the membranes in the range *HZD-3* > *HZD-2* > *HZD-1* are evidenced by both higher ion-exchange capacity and reduced pore sizes.

The membrane selectivity towards anions in weakly acid media was estimated by measurements of the membrane potential. The voltage in the system Ag/AgCl, KCl/ inner solution/membrane/outer solution/KCl, AgCl/Ag reached a constant level after a period of time varying from 5 min with *HZD-3* to 30 min with *HZD*-1. The membranes containing the ion-exchanger seem to act as a barrier to both ions. Equalisation of solution concentration on both sides of the membrane cannot occur. The results suggest that the membranes containing *HZD* are anion-selective and that the recorded voltage corresponds to the membrane potential (E_m).

In the case of an inert matrix, the voltage was found to increase up to zero within approximately 5 min, indicating the absence of selective properties.

For ideally selective membranes the potential difference is given by [14]:

$$E_m = -\frac{RT}{z_i F}\ln\frac{a_{i,1}}{a_{i,2}}, \qquad (3)$$

The subscripts "1" and "2" correspond to the activity of ions in less and more concentrated solutions, respectively, and the subscript "i" corresponds to the potential-determining ion. Assuming that the activities of Cl^- ions can be approximated by their concentrations, we get $E_m = -18$ mV. It can be seen that the values of the membrane potential are below the calculated magnitude. The difference between the measured and calculated values is evidently caused by Donnan potentials due to diffusion of co-ions (H^+) through the membranes. This suggests that larger amounts of ion-exchanger species in ceramic membranes improved selectivity towards anions in acidic media.

At the same time increasing the amount of ion-exchanger in the membranes led to lower conductivity due to reduced pore size. Lower ion concentrations also resulted in reduced membrane conductivity. This is caused by the reduced conductivity of the solution inside the pores on the one hand and a decrease in the degree of dissociation of the functional groups on the other hand.

3.2. *Investigation of Cr(VI) transport through composite ceramic membranes*

For all cases, the catholyte was a $K_2Cr_2O_7$ solution of various concentrations. The anolyte was either a dilute NaOH solution, or a sulfuric acid solution, or eventually mixed sodium sulfate-sulfuric acid media, as shown in Table 2.

3.2.1. *Effect of anolyte composition*

HZD-2 membrane was chosen for this series of experiments based on the results mentioned above. Increasing the amount of ion-exchanger in membranes causes an improvement in their selective properties but simultaneously leads to an increase in resistance. Thus *HZD-2* membrane can be considered as an optimal variant.

The solution passing through the cathode compartment contained 2 mol m^{-3} Cr(VI). The initial pH of this solution was 7.

3.2.1.1. Acidity of the anolyte. The effect of anolyte acidity on Cr(VI) transport was studied. The runs were performed at 2 A m^{-2}. When the initial pH was 3 or higher, aliquots of 0.1 M NaOH solution were added to

Table 1. Characteristics of the membranes containing ion-exchange component

Sample	Average pore diameter, nm	Full anion-exchange capacity towards Cl^-, mmol g^{-1} (determined in acidic medium)	Full cation-exchange capacity towards Na^+, mmol g^{-1} (determined in alkaline medium)	Membrane potential, mV (5×10^{-2}/1×10^{-3} M HCl)	Surface conductivity, Ohm^{-1} m^{-2}	
					5×10^{-2} M H_2SO_4	1×10^{-3} M H_2SO_4
HZD-1	180	4.5×10^{-3}	4.4×10^{-3}	11.0	4010	402
HZD-2	140	9.2×10^{-3}	9.3×10^{-3}	13.5	1508	142
HZD-3	83	1.0×10^{-2}	1.0×10^{-2}	14.9	1059	100

Table 2. Dependence of catholyte pH and cell voltage on anolyte composition

Initial anolyte pH	Initial anolyte composition	Catholyte pH	E/V at the start of the experiment (excluding start-up effect)
11.8	1×10^{-2} M NaOH	10.2	3.5
3	5×10^{-3} M Na_2SO_4 acidified with H_2SO_4	6.3	4.5
2	5×10^{-3} M Na_2SO_4 + 5×10^{-3} M H_2SO_4	5.8	2.8
2	5×10^{-3} M H_2SO_4	5.8	2.8
1.8	1×10^{-2} M H_2SO_4	5.6	2.6
1.4	5×10^{-2} M H_2SO_4	5.5	2.5
1.3	0.1 M H_2SO_4	5.5	2.5

the anolyte during electrodialysis to maintain the pH near its initial level. In the other cases the anolyte pH remained nearly unchanged and no alkali solution was added.

As shown in Table 2, the pH at the outlet of the cathode chamber decreased with increasing acid content in the anolyte: the pH at the outlet was below 7 with all the acidic anolytes tested. Acidification of the catholyte was evidently caused by H^+ ion transport through the membrane, as reported for both homogeneous [15] and heterogeneous [16] organic anion-exchange membranes. On the other hand, OH^- ions generated at the cathode were partially neutralised by H^+ ions formed at the membrane surface by water splitting [17]. When the anode compartment was filled with NaOH solution, the catholyte was alkalised.

The number of moles of Cr(VI) species in the anolyte ($n_{Cr,a}$) and the quantity of Na^+ ions in the catholyte ($n_{Na,c}$) are plotted in Figure 2*vs* electrodialysis time (τ) for the case of 0.01 M NaOH anolyte solution. It can be seen from the figure that the rate of Cr(VI) transport to the anolyte is much lower than the rate of Na^+ cation migration to the catholyte. Moreover, the ion transport rates were relatively constant, allowing the flux of Cr(VI) ions through the membrane ($N_{Cr,m}$) to be calculated from the slope of a $n_{Cr,a}$ *vs* τ plot:

$$N_{Cr,m} = \frac{1}{A}\frac{dn_{Cr,a}}{d\tau} \tag{4}$$

where A is the effective membrane area. The flux of sodium ions through the membrane ($N_{Na,m}$) was calculated similarly. The $n_i - \tau$ dependencies were then disregarded and the results were given and discussed in terms of ion fluxes.

Fluxes N_i are plotted *vs* anolyte pH in Figure 3. Decreasing the anolyte pH caused higher Cr(VI) flux through the membrane. At the same time a considerable sodium ion flux to the catholyte was found in alkaline media. Decrease of the anolyte pH led to a lower rate of Na^+ transport to the cathode compartment. During electrodialysis the cell voltage (E) was observed to decrease slightly due to an increase in anolyte conductivity. No change in anolyte volume was observed.

A spectrophotometric analysis of both catholyte and anolyte [18] showed that the concentrations of Cr(III) ions were below the detection limit (0.1 mol m^{-3}). The same was observed in the other series of experiments described below.

For alkaline anolyte solutions, a small amount of K^+ (0.25 mol m^{-3}) was detected in the anode compartment after 8 h of electrodialysis. This was evidently caused by diffusion of cations from the cathode compartment through the membrane. Since the Na^+ concentration in the anolyte was much higher than the K^+ concentration, the current was mainly provided by sodium ion transport to the catholyte. With acidic anolytes, practically no K^+ ions penetrated into the anode compartment.

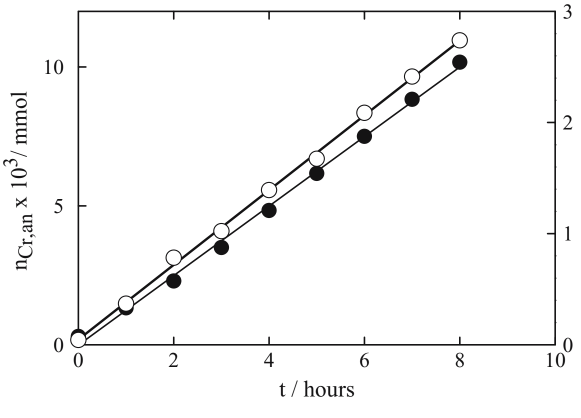

Fig. 2. Cr(VI) amount in the anolyte (•) and Na^+ amount in the catholyte (○) over time of electrodialysis using *HZD-2* membrane. The anolyte pH was kept near 11.8, the pH of the solution in the cathode compartment reached 10.2, i = 2 A m^{-2}. The initial Cr(VI) concentration in the catholyte was 2 mol m^{-3}.

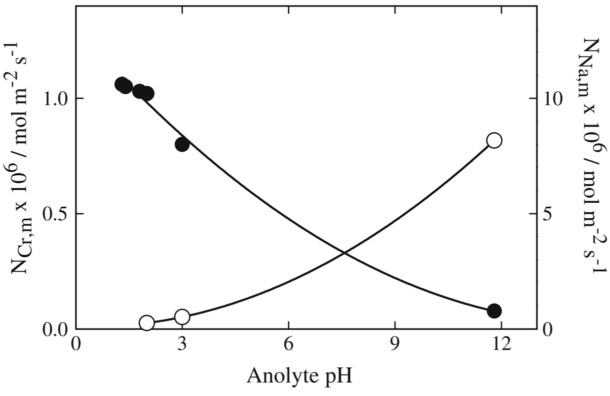

Fig. 3. Cr(VI) flux to the anolyte (•) and Na^+ flux to the catholyte (○) depending on the anolyte pH. The cathode and anode compartments were separated with *HZD-2* membrane, i = 2 A m^{-2}. The initial Cr(VI) concentration in the catholyte was 2 mol m^{-3}.

Three experiments were also performed under open circuit conditions. 0.01 M NaOH, 5×10^{-3} M Na_2SO_4 or 5×10^{-3} M H_2SO_4 were circulated through the anode compartment. The other conditions were similar to those given above. After 8-hour runs, the amount of Cr(VI) in the anode compartment was found to be 5×10^{-3} (alkaline anolyte), 0.01 (neutral anolyte), and 0.02 (acidic anolyte) mmol. These amounts are two orders of magnitude lower than the corresponding amount of Cr(VI) transported to the anolyte within the same period at 2 A m^{-2}.

3.2.1.2. Initial chromate content in the anolyte. Several experiments were performed with varying initial chromate concentration in a 5×10^{-3} M H_2SO_4 anolyte solution. Electrodialysis was carried out at 2 A m^{-2} when the initial Cr(VI) concentration in the anolyte was 10 mol m^{-3}. For the highest initial Cr(VI) concentrations (250 mol m^{-3}) the current density was fixed at 10 A m^{-2}. Runs using chromate-free solutions of sulphuric acid in the anode chamber were also carried out for comparison.

For all cases, the amount of chromate in the anode compartment increased during the run and the Cr(VI) flux through the membrane was found to be independent of the initial chromate concentration in the anolyte at different currents (Table 3).

The increase in current density was found to result in higher catholyte pH, which increased from 5.6 at 2 A m^{-2} to 6.4 at 10 A m^{-2}. This is caused by a higher H^+ consumption at the cathode (due to H_2 formation) than the role of H^+ transport though the membrane. The corresponding cell voltage at initial time was 2.8 and 6.8 V. No change in the anolyte volume was observed and there was no diffusion of K^+ into the anolyte.

3.2.2. *Effect of catholyte composition*

The influence of H^+ (OH^-) and Cr(VI) concentrations in the catholyte on the efficiency of chromate transport was studied. A 5×10^{-3} M H_2SO_4 solution was circulated through the anode compartment, and the membrane was made of *HZD-2* material.

In the first series of the experiments the catholyte acidity was varied. The solutions containing 2 mol m^{-3} Cr(VI) were previously acidified with H_2SO_4 to fix their pH at the desired value between 2 and 4, or alkalized with NaOH up to pH 11. One run was performed with a pure Cr(VI) solution without addition of acid or alkali. Electrodialysis was performed at 2 and 4 A m^{-2}.

With the solutions, which were previously acidified or alkalized, pH was not changed significantly by the ion exchange in the cell. As shown in Figure 4, $N_{Cr,m}$ increased for pH ranging from 2 to 3.5, and a sharp maximum was observed at pH 3.5. For higher catholyte pH, the rate of chromate transport to the anode compartment decreased regularly with pH. When an alkaline solution was passed through the cathode compartment, the cell voltage increased dramatically (Figure 5).

The anolyte volume remained constant with time. With alkaline solution in the anode chamber, a small amount of K^+ (0.04 mmol) was found in this compartment after 8 h of electrodialysis, whereas practically no K^+ ions were transferred at neutral/acidic pH.

Table 3. Effect of the initial Cr(VI) content the anolyte on the chromate transport through *HZD-2* membrane

Initial Cr(VI) content in the anolyte/mmol	i/A m^{-2}	$N_{Cr,m} \times 10^5$ / mol m^{-2} s^{-1}
–	4	0.34
1.5	4	0.32
–	10	2.27
50	10	2.31

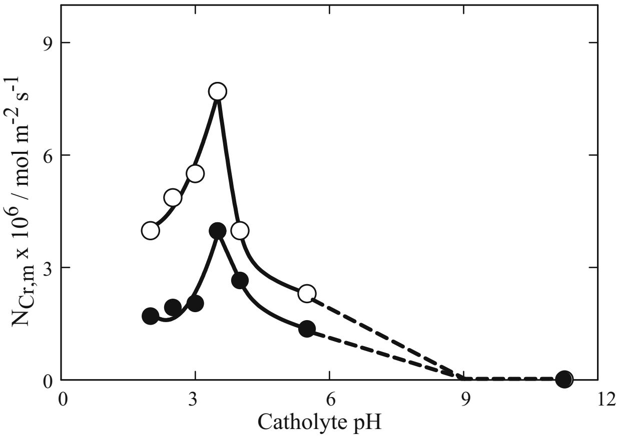

Fig. 4. Cr(VI) flux through *HZD-2* membrane at 2 (•) and 4 (○) A m^{-2} as a function of catholyte acidity. The anode compartment was filled with a 5×10^{-3} M H_2SO_4 solution, the initial Cr(VI) concentration in the catholyte was 2 mol m^{-3}.

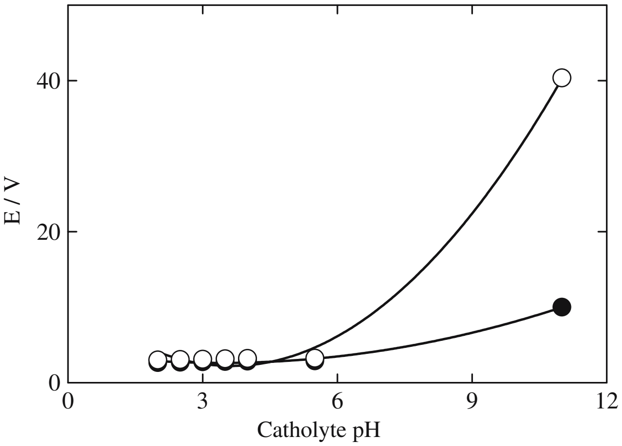

Fig. 5. Cell voltage at 2 (•) and 4 (○) A m^{-2} as a function of catholyte pH. The cathode and anode compartments were separated with *HZD-2* membrane. The anode compartment was filled with a 5×10^{-3} M H_2SO_4 solution, the initial Cr(VI) concentration in the catholyte was 2 mol m^{-3}.

In the second series of the experiments the chromium concentration in the catholyte was varied. The initial Cr(VI) content in the catholyte solution was varied, and the current density was fixed at 2 A m^{-2}.

Figure 6 shows the flux of chromate anions as a function of their concentration in the catholyte ($C_{\mathrm{Cr,c}}$). Increase in $C_{\mathrm{Cr,c}}$ leads to increased transport rate to the anolyte. It should be noted that the $N_{\mathrm{Cr,a}} - C_{\mathrm{Cr,c}}$ dependence is practically linear (only one point gives a slight deviation).

The pH of the solution leaving the cathode compartment reached approx. 5.5. No changes in the anolyte volume were observed and no potassium ions were detected in the anode compartment.

3.2.3. *Effect of current density*

The influence of the applied current density in the range 2–10 A m^{-2} on the chromate flux through *HZD-1*-*HZD-3* membranes was also investigated. The initial concentration of Cr(VI) ions in the solution circulating in the catholyte was fixed at 2 mol m^{-3}. A 5×10^{-3} M H_2SO_4 solution was circulated through the anode compartment.

The variation of the Cr(VI) flux with the applied current density is shown in Figure 7. It can be seen that in all cases the $N_{\mathrm{Cr,a}}$ vs. i curves exhibit three sections: a slow increase in $N_{\mathrm{Cr,a}}$ in the range 2–4 A m^{-2}, followed by a sharp rise in the range 4–8 A m^{-2} and a plateau of transport rate for higher current densities.

The cell voltage increased proportionally with applied current and pH of the solution leaving the cathode compartment also increased with the current density. For instance, in the case of *HZD-2* membrane the pH was changed from 5.3 to 6 (2–4 A m^{-2}) from 6 to 7 (5–8 A m^{-2}) and from 7 to 7.4 (8–10 A m^{-2}); as was explained in section 3.2.1.2 (the initial pH was constant). Similar behaviour was established for other membranes.

No pH change and no K^+ transport to the anolyte were observed in the experiments.

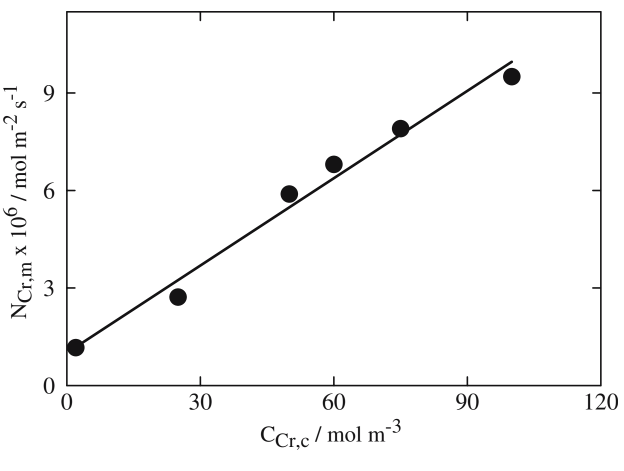

Fig. 6. Cr(VI) flux through *ZHD-2* membrane as a function of chromium content in the catholyte. The anode compartment was initially filled with a 5×10^{-3} M H_2SO_4 solution, i = 2 A m^{-2}.

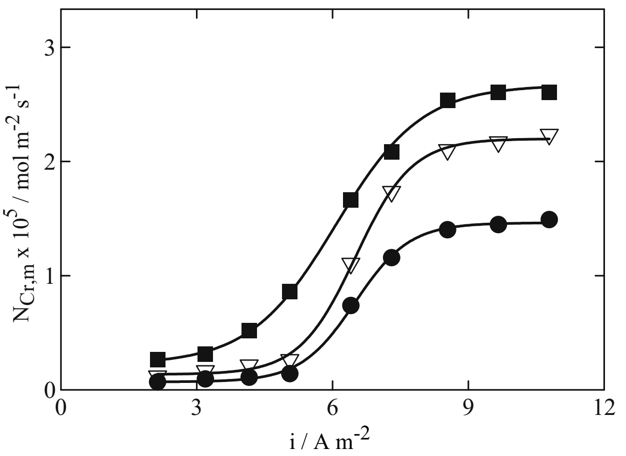

Fig. 7. Cr(VI) flux through *HZD-1* (●), *HZD-2* (▽), *HZD-3* (■) membranes as a function of applied current. The anode compartment was initially filled with a 5×10^{-3} M H_2SO_4 solution, Cr(VI) concentration in the catholyte was 2 mol m^{-3}, the pH of the solution at the outlet of cathode compartment was 5.3–7.0 depending on applied current.

4. Discussion

As expected, the membranes containing amphoteric *HZD* exhibit anion-exchange properties in acidic media and cation-exchange properties in alkaline solutions. At the same time, alkalization of the catholyte and acidification of the anolyte results in a decrease in ionic permeability. In this case, the membrane acts as bipolar one: the membrane is charged negatively from the direction of the cathode compartment while the positively charged side of the membrane is placed in the anode compartment. This causes a sharp increase in cell voltage (as seen from Figure 6) to provide permeability of ions through the membrane for the sake of electroneutrality in the system.

The results were quantitatively examined as follows. The flux of ions through the membrane ($N_{\mathrm{Cr,m}}$) is related to the current density [4]. On the other hand, under forced convection conditions, flux $N_{\mathrm{Cr,m}}$ is governed by migration in the bulk of the solution and diffusion through the solution near the membrane surface. The overall material balance of the electrodialysis process may be expressed as:

$$N_{\mathrm{Cr,m}} = \frac{it_{\mathrm{Cr,m}}}{z_{\mathrm{Cr}}F} = \frac{it_{\mathrm{Cr,s}}}{z_{\mathrm{Cr}}F} + k_{\mathrm{Cr}}\left(C_{\mathrm{Cr,s}} - C^{0}_{\mathrm{Cr,s}}\right). \qquad (5)$$

The migration and diffusion terms of Equation (6) are related to each other [19]:

$$k_{\mathrm{Cr}}\left(C_{\mathrm{Cr,s}} - C^{0}_{\mathrm{Cr,s}}\right) = \gamma \frac{It_{\mathrm{Cr,s}}}{z_{\mathrm{Cr}}F}, \qquad (6)$$

where γ is the ratio of anion and cation valencies (for the solution without supporting electrolyte). The flux of Cr(VI) ions through the ideally selective membrane is proportional to the applied current. Under limiting conditions $C^{0}_{\mathrm{Cr,s}} = 0$. Thus:

$$N_{Cr,m} = (1+\gamma)k_{Cr}C_{Cr,s} \tag{7}$$

In this case the ion transport through the membrane does not depend on the current: the Cr(VI) flux is determined by hydrodynamic parameters of the electrodialysis system and the concentration in the catholyte. Thus, if $C_{Cr,s}$ is maintained constant, $N_{Cr,m}$ reaches a stable value and does not increase with further current increase under convectionless conditions. Analysis of the data of Figure 7 allows the limiting current density provided by Cr(VI) ions ($i_{Cr,lim}$) to be estimated as 8 A m^{-2}.

The value of limiting current density can also be obtained theoretically using a mass transport coefficient value calculated from correlation equations. In the case of laminar flow through a vertical column, the mass transport coefficient can be estimated using the Levèque equation [20]:

$$Sh = 1.62\left(ReSc\frac{d}{L}\right)^{0.33}. \tag{8}$$

Here $Sh = \frac{k_{Cr}d}{D_{Cr,s}}$, $Re = \frac{du}{\nu}$, $Sc = \frac{\nu}{D_{Cr,s}}$. From a cross-section area of the cathode compartment of 8.8×10^{-5} m^2, $u = 1.07 \times 10^{-2}$ m s^{-1}. The following values of physico-chemical parameters for dilute solutions at 298 K were used: $D_{Cr} = 1.13 \times 10^{-9}$ m^2 s^{-1}, $\nu = 8.99 \times 10^{-7}$ m^2 s^{-1} [21], $d = 2 \times 10^{-3}$ m, $L = 1.3 \times 10^{-2}$ m, the *Sc, Re* and *Sh* numbers were estimated to be 795, 23.8, and 11.5 respectively. Thus the mass transport coefficient was estimated to be 6.49×10^{-6} m s^{-1}.

Since there is no supporting electrolyte in the catholyte, migration has to be taken into account in addition to diffusion. Then the limiting current (related to the outer surface area of membrane), which is caused by Cr(VI) transport through the membrane, is given by [19]:

$$i_{Cr,lim} = (1+\gamma)z_{Cr}Fk_{Cr}C_{Cr,s}, \tag{9}$$

At 2-4 A m^{-2} (sections of slowly increasing chromate flux in Figure 7) the solution pH in the cathode compartment did not exceed 6, and the initial Cr(VI) concentration was 2 mol m^{-3}. Cr(VI) ions are mainly in the form of $HCrO_4^-$ ($\gamma = 1$) under these conditions [22]. Thus $z_{Cr} = 1$, and hence $\gamma = 1$ (with K^+ cations acting as counter-ions), and $i_{Cr,lim} = 2.5$ A m^{-2}. At 8–10 A m^{-2} (plateau sections of the plots in Figure 7), the catholyte pH was above 7. Consequently, it may be suggested that CrO_4^{2-} species predominate in the solution [22]. Therefore $z_{Cr} = 2$, and hence $\gamma = 2$. The limiting current, which corresponds to chromium transport, is 7.5 A m^{-2}. This value is in good agreement with the experimental value obtained using the data of Figure 7 (8 A m^{-2}).

The pH of the catholyte under limiting current conditions was above 7, and Cr(VI) concentration was 2 mol m^{-3}; it may be suggested that CrO_4^{2-} species predominate in the solution [22]. Thus $C_{Cr,s} = 2$ mol m^{-3}, $z_{Cr} = 2$, and hence $\gamma = 2$ (with K^+ cations acting as counter-ions). According to (9), the limiting current, which corresponds to chromium transport, is 7.5 A m^{-2}. This value is in good agreement with the experimental value obtained using the data of Fig. 7 (8 A m^{-2}). Hence a sharp increase in chromium transport rate within the interval of 4–8 A m^{-2} may be caused by the $HCrO_4^- \rightarrow CrO_4^{2-}$ transition.

At 8 A m^{-2}, the transport numbers of Cr(VI) were estimated to be 0.33 (*HZD-1*), 0.51 (*HZD-2*), 0.63 (*HZD-3*). Thus increasing the amount of ion-exchanger in ceramic membranes results in an improvement of electrodialysis efficiency. Deviation of $t_{Cr,m}$ from 1, when the current does not exceed the limiting value, is also typical of organic anion-exchange membranes.

Acidification of the catholyte improves the chromate transport through the membrane. However, when the concentrations of Cr(VI) and sulphate-bisulfate anions in the catholyte become commensurable, $N_{Cr,m}$ decreases due to higher flux of other anions. This may explain the maximum shown in Figure 4, which illustrates the effect of catholyte pH. The $t_{Cr,m}$ magnitude reaches approximately 0.2, when the chromate flux reaches the maximum value. Taking into consideration the forms of chromate anions in solutions with different pH, the transport number values were calculated (Figure 8). At pH < 6 and for a Cr(VI) concentration of 2 mol m^{-3}, $HCrO_4^-$ species predominate in the solution, thus $t_{Cr,m} \approx 0.2$ in the peak region (pH 3.5). At the same time CrO_4^{2-} ions (besides OH^- ions) are mainly present in alkaline solution ($z_{Cr} = 2$), which allowed estimation of the transport number of these species (Figure 8).

As shown in Figure 6, increase in Cr(VI) concentrations in the catholyte also leads to an improvement in chromate transport to the anode compartment. At pH < 6 and a Cr(VI) concentration of 100 mol m^{-3} and lower, $HCrO_4^-$ species predominate in the solution. Thus the $t_{Cr,m}$ value increases from 0.044 to 0.44 for the *HZD-2* membrane, if the Cr(VI) concentration in the

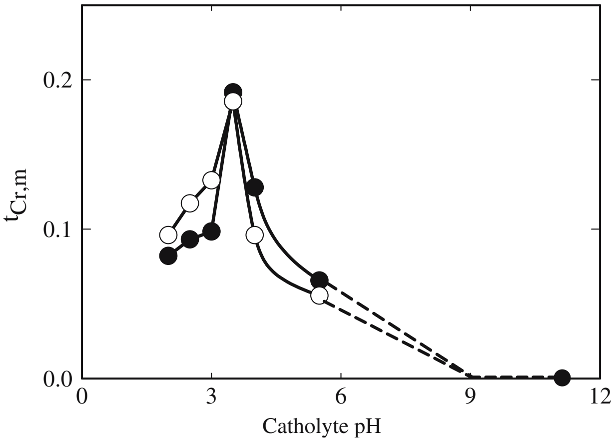

Fig. 8. Cr(VI) transport number through *HZD-2* membrane at 2 (•) and 4 (■) A m^{-2} as a function of catholyte acidity. The anode compartment was initially filled with a 5×10^{-3} M H_2SO_4 solution, Cr(VI) concentration in the catholyte was 2 mol m^{-3}.

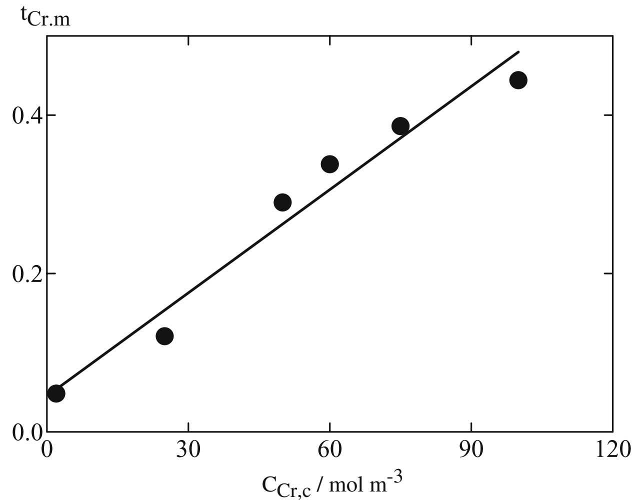

Fig. 9. Cr(VI) transport number through *HZD-2* membrane as a function of chromium content in the catholyte. The anode compartment was filled with a 5×10^{-3} M H_2SO_4 solution, $i = 2$ A m^{-2}.

cathode compartment increases from 2 to 100 mol m^{-3} (Figure 9).

5. Conclusions

Ceramic membranes containing hydrated zirconium dioxide (HZD) as an ion exchange component were shown to be permeable to anions in acidic media while exhibiting cation-exchange properties in alkaline media.

The main characteristics of Cr(VI) transport through membranes have been investigated. Larger quantities of ion-exchanger species afford significant gains in electrodialysis efficiency. The Cr(VI) transport numbers have been estimated to be in the range 0.33–0.63 under limiting current conditions. Increasing the concentration of H^+ or Cr(VI) ions in the solution to be purified also causes an increase in the rate of Cr(VI) ion transport through the membrane.

The present work showed that the membranes developed can be successfully used for the concentration of hexavalent chromium from solutions due to their selectivity towards anions on the one hand and high chemical stability on the other hand. However, increase in the amount of ion-exchanger in the membrane results in a decrease in electrical conductivity. The conductivity of a ceramic membrane is lower by 1–2 orders of magnitude than that of modern membranes produced industrially. Thus improvement of their conducting properties must be achieved.

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