

Chromium(III)-Selective Electrodes Based on Titanium Dichalcogenides Intercalated with Chromium

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Abstract—Solid-contact chromium-selective film electrodes were prepared on the basis of titanium diselenide and titanium ditelluride intercalated with chromium. It was found that the titanium diselenide-based electrode with the lowest concentration of the intercalant ($\text{Cr}_{0.1}\text{TiSe}_2$) exhibits the best properties and provides the determination of 5×10^{-5} – 1×10^0 M chromium(III) in the pH range 2.75–4.7. The slope of the electrode function for all chromium-selective electrodes depends on the pH of the solution and is close to the theoretical slope for the singly charged $\text{Cr}(\text{OH})_2^+$ ion. It was demonstrated that chromium-selective electrodes can be used as indicator electrodes in determining chromium(III) by direct titration with the potentiometric detection of the titration end-point using EDTA and KMnO_4 as titrants.

The use of chromium in industry is associated with environmental pollution, which in turn calls for the development of reliable, simple, portable, and inexpensive diagnostic tools. Among such tools are solid-state ion-selective electrodes, which provide the determination of both Cr(VI) and Cr(III). To determine Cr(VI), it was proposed to use solid-state chromium-selective electrodes based on chalcogenide glasses [1]. As far as we know, solid-state electrodes for determining Cr(III) have not been developed.

In this work, we examined the possibility of developing solid-state electrodes for determining chromium(III) using titanium dichalcogenide intercalated with chromium as the active substance.

The main requirements for active substances of solid-state ion-selective electrodes are weak binding of the analyte ions by the matrix lattice (the analyte ion should easily be exchanged between the active element and the test solution), the existence of mixed ionic–electronic conductivity sufficiently high for an equilibrium between the solution/membrane and the membrane/lead interfaces be attained, and selectivity to the analyte ion in the presence of foreign ions [2, 3]. Intercalates, including titanium chalcogenides Cr_xTiX_2 ($X = \text{Se}, \text{Te}$) perfectly meet the above requirements. The possibility of the reversible introduction of an intercalant [Cr(III) in this work] is due to weaker bonds between Cr(III) and the matrix lattice compared to the bonds in the lattice. The proposed materials possess relatively high conductivity [4], which is no lower than 100 S/cm. The selectivity of Cr_xTiX_2 for Cr(III) ions is, probably, due to the existence of a correlation between the deformation energy of the lattice and the ionization potential of the intercalated ion [5]. This correlation is due to the fact that the intercalation of a foreign ion into a material preliminarily intercalated with Cr(III) requires addi-

tional work for the deformation of the lattice, which is unnecessary for the exchange of Cr(III) ions.

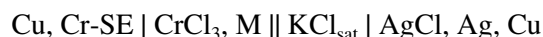
EXPERIMENTAL

Titanium dichalcogenides Cr_xTiX_2 ($X = \text{Se}, \text{Te}$) intercalated with chromium were prepared from individual elements using three-step ampoule synthesis. The materials prepared were used as active elements of solid-state ion-selective electrodes. Titanium purified by the iodide method (purity 99.95%), tellurium purified by triple vacuum distillation (purity no worse than 99.9%), high-purity selenium 19-5 (purity 99.9%), and chromium of 99.9% purity were used in the synthesis. At the first step, TiTe_2 and TiSe_2 were prepared by sintering elements for 10 days at 950°C in quartz ampoules pumped down to 10^{-5} torr. Next, the contents of the ampoules was taken out and comminuted; the unreacted titanium was determined; the reaction product was pressed for a better contact between the phases and sintered again in evacuated quartz ampoules at 800°C for 10 days. The temperature at the second was lower than at the first step in order to prevent the substitution of chromium for titanium in the matrix lattice, like it was observed for iron intercalates [6]. Under these conditions, the material obtained after single sintering cycle was usually inhomogeneous. Because of this, the material after the second step was again comminuted, pressed, and subjects to homogenization sintering under the same conditions. The material obtained after the second cycle was homogeneous to within the accuracy of X-ray structural analysis (DRON-3M, CuK_α , graphite monochromator). The electric conductivity measured by the conventional four-probe method was 500–800 S/cm, depending on the intercalant concentration and the nature of the chalcogen. The ionic

conductivity estimated by the Nernst–Einstein equation using times necessary for a homogeneous state be attained during the sintering was 10^{-7} to 10^{-10} S/cm. Thus, the contribution of the ionic conductivity to the total conductivity of the material was insignificant.

The measurements were performed using a film active element. To prepare this element, a mixture of Cr_xTiX_2 ($X = \text{Se}, \text{Te}$) with a polystyrene solution in methyl ethyl ketone was applied on a lead, which was made by tipping a glass rod with Wood alloy, and dried. The procedure for the electrode preparation was described in [7].

The electrode properties of the chromium-selective electrode (Cr-SE) were studied by measuring the emf of the circuit



using a EV-74 and an I-130M potentiometers operating in the millivoltmeter mode. The pH of the solutions was controlled with an I-130 potentiometer with a glass electrode. The measurements were performed at $20 \pm 2^\circ\text{C}$. Before measurements, the electrodes were washed in distilled water acidified to certain pH until a constant potential was attained; the circuit was closed. If the electroanalytical properties of the electrodes changed after long work, the electrodes were conditioned in a 10^{-3} M solution of CrCl_3 or $\text{Cr}_2(\text{SO}_4)_3$ for 30 min at the closed electric circuit and, then, washed in distilled water for 20 min until a constant potential was attained. The electrodes were stored dry between the measurements.

To obtain reproducible results, stock 1 M solutions of CrCl_3 and $\text{Cr}_2(\text{SO}_4)_3$ before use were allowed to stand for no shorter than 24 h. It was necessary because the pH of freshly prepared solutions gradually changed from 3.5 to 2.5 with the color of the solution changing from green to violet, in good agreement with the reported data on the state of chromium(III) ions in the solution [8].

The dependence of the potential of a chromium-selective electrode on the concentration of Cr(III) was studied in solutions of CrCl_3 or $\text{Cr}_2(\text{SO}_4)_3$ in the concentration range 1×10^{-6} to 1×10^0 M at a constant pH of 2.0–4.7. The selectivity of the electrodes was estimated using a constant interfering ion concentration ($c_{\text{Me}} = 1 \times 10^{-3}$ M).

In the titrimetric determination, chromium was titrated with a 0.05 M EDTA solution (pH 4.0; acetate buffer solution) and a solution of KMnO_4 ($c(1/5\text{KMnO}_4) = 0.01$ M) (pH 3.2). The titration endpoint was determined graphically from integral [E (mV) vs. V (mL)] and differential [dE/dV vs. V (mL)] titration curves. Calibration plots were constructed on the coordinates the number of the titrant (in millimoles) against the number of chromium (in millimoles).

RESULTS AND DISCUSSION

Previously [9], it was shown by the example of Co_xTiTe_2 that the electrode properties of ion-selective intercalant-based electrodes depend on the concentration of the intercalant being optimal for the compound with the composition close to the percolation threshold $\text{M}_{0.25}\text{TiX}_2$ (M is intercalant). This composition forms a boundary between the states of dilute and concentrated solid solutions. To check whether the chromium(III) intercalant behaves similarly, we studied chromium(III)-selective electrodes based on a number of titanium diselenides and ditellurides intercalated with chromium and differing in the intercalant concentration.

The electrode characteristics of chromium-selective electrodes based on $\text{Cr}_{0.1}\text{TiSe}_2$ (electrode 1), $\text{Cr}_{0.25}\text{TiSe}_2$ (electrode 2); $\text{Cr}_{0.33}\text{TiSe}_2$ (electrode 3); and $\text{Cr}_{0.25}\text{TiTe}_2$ (electrode 4) were determined in solutions of CrCl_3 at pH 3.5. The results obtained are summarized in Table 1. The plots of electrode functions are shown in Fig. 1. The results presented indicate that the linearity range of the electrode function for chromium-selective electrodes becomes wider as the intercalant concentration is decreased, and electrode 1 ($\text{Cr}_{0.1}\text{TiSe}_2$) exhibits the best electrode properties. For this electrode, the electrode function is linear in the range of chromium(III) concentrations from 5×10^{-5} to 1×10^0 M. The detection limit for cobalt in pure solutions for this electrode was 1.6×10^{-5} M.

The slope of the electrode function for all chromium-selective electrodes in the pH range 2.5–4.5 was higher than the theoretical slope (19 mV/pc) for a triply charged Cr(III) ion and increases with pH to the theoretical slope (59 mV/pc) for the singly charged $\text{Cr}(\text{OH})_2^+$ ion. Such pH dependence of the slope of the electrode function is due to the fact that chromium(III) ions undergo hydrolysis [10–12]. The authors of [11] believe that all steps of hydrolysis of chromium(III) are plausible at pH of about 0.4. Therefore, chromium(III) in the studied pH region occurs as hydroxo species.

As it follows from the data presented in Table 1 and Fig. 2, the pH dependence of the slope of the electrode function is almost independent of the electrode material. This confirms the conclusion that the slope of the electrode function is determined only by the state of chromium ions in the solution.

The plots the slope of the electrode function of chromium-selective electrodes based on titanium diselenide and ditelluride of the composition $\text{Cr}_{0.25}\text{TiSe}_2$ and $\text{Cr}_{0.25}\text{TiTe}_2$ vs. pH (curves 4 and 5 in Fig. 2) agree well with the distribution pattern for chromium hydroxo complexes as a function of pH (curves 1–3), which was calculated based on the results of the spectrophotometric study of the complexation of chromium(III) with hydroxide ions [13]. According to this study, chromium(III) in solutions of pH 2.5–4.5 occurs mainly as

Table 1. Electrode properties of chromium-selective electrodes

Electrode	Test solution	Linearity range of the function $E = f(\text{pCr})$, M	Slope of electrode function, mV/pCr	Working pH range
Cr _{0.1} TiSe ₂ (electrode 1)	CrCl ₃ , pH 3.5	5×10^{-5} – 1×10^{-0}	$-(57 \pm 2)$	2.75–4.7
Cr _{0.25} TiSe ₂ (electrode 2)	CrCl ₃ , pH 3.5	1×10^{-3} – 1×10^{-1}	$-(60 \pm 2)$	3.0–4.5
Cr _{0.33} TiSe ₂ (electrode 3)	CrCl ₃ , pH 3.5	1×10^{-3} – 1×10^{-1}	$-(54 \pm 2)$	3.0–3.75
Cr _{0.25} TiTe ₂ (electrode 4)	CrCl ₃ , pH 3.5	5×10^{-4} – 1×10^{-1}	$-(50 \pm 2)$	3.0–4.5

hydroxo complexes Cr(OH)²⁺ and Cr(OH)₂⁺. The slope of the electrode function in the vicinity of pH 3.75 is of special interest. In this region, the electrode behavior is unstable. This point coincides with the point of the coexistence of three different chromium(III) hydroxo complexes in the distribution pattern (Fig. 2). At the same time, it should be noted that the data on the chromium speciation in solutions reported in [13] were not confirmed in the later works [10, 12], in which the triple point was not observed. This difference in the distribution patterns of chromium(III) hydroxo complexes is, probably, due to a difference in the concentrations of solutions studied by the authors of the above works. In [13], hydroxo complexes were studied in dilute solutions, whereas the authors of [12] used solutions occurring in equilibrium with the Cr(OH)₃ precipitate. In this work, we used dilute solutions; therefore, it seems quite natural that the results obtained are in good agreement with the data of [13].

A comparison of the electrode characteristics of chromium-selective electrodes based on titanium diselenide and ditelluride with equal intercalant concentra-

tions (Cr_{0.25}TiX₂) at pH 3.5 (Fig. 1, curves 2 and 4, and Table 1) indicates that the electrode function of the titanium ditelluride-based electrode is linear in a slightly wider range. This is, probably, due to less ionic bonding of the intercalant with the matrix lattice (0.09 for the ditelluride compared to 0.18 for the diselenide according to Pauling [14]) and, therefore, the lower solubility of the ditelluride.

The electrode functions of chromium-selective electrodes in sulfuric acid solutions exhibited narrower linearity ranges than those in hydrochloric acid solutions. For electrodes 2–4, the linearity range of the electrode function was 1×10^{-2} to 1×10^{-1} M and for electrode 1, 1×10^{-4} to 1×10^{-1} M. It should be noted that the slope of the electrode function in sulfuric acid solutions was lower than that in hydrochloric acid solutions, which may be due to the formation of more stable sulfate complexes of chromium(III) [8].

In going from water to chromium(III) solutions with concentrations 1×10^{-6} to 1×10^{-5} M, the response time changed from 5 to 2 min; for solutions with concentrations above 1×10^{-4} M, the response time was shorter

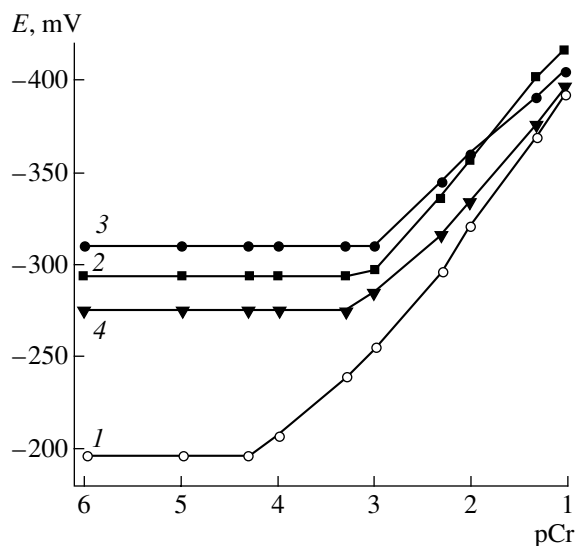


Fig. 1. Electrode functions of chromium-selective electrodes based on Cr_xTiX₂: (1) Cr_{0.1}TiSe₂ (electrode 1); (2) Cr_{0.25}TiSe₂ (electrode 2); (3) Cr_{0.33}TiSe₂ (electrode 3); (4) Cr_{0.25}TiTe₂ (electrode 4); pH 3.5.

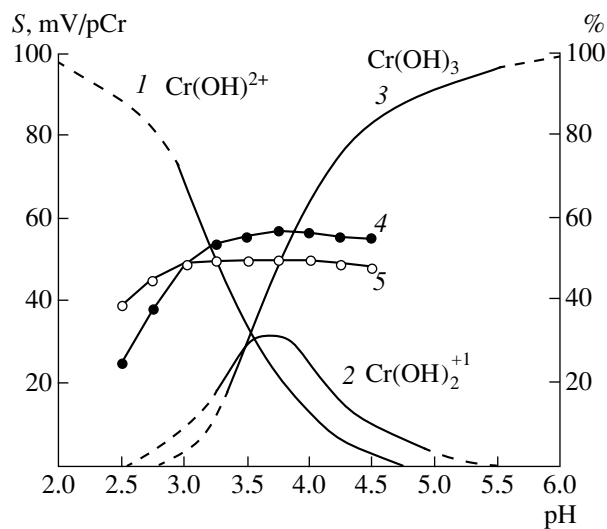


Fig. 2. Distribution pattern for chromium(III) hydroxo complexes [13] (curves 1–3) and the slopes of electrode functions of electrodes 2 and 4 as functions of pH (curves 4 and 5).

than 1 min both in hydrochloric and sulfuric acid solutions. The potential drift within 24 h was no more than ± 2 mV; the detection limit for chromium in this case remained unchanged. After long work, the electrode potential shifted to more negative values at a rate of about 10 mV per month. The service life of the electrodes was no shorter than 550 h of continuous work. For the period of investigations (more than 1.5 years), the electrode retained its analytical properties when stored dry between measurements.

The potentiometric selectivity coefficients determined using constant concentrations of interfering ions ($c_{Me} = 1 \times 10^{-3}$ M) are presented in Table 2. These data are indicative of the insufficient selectivity of chromium-selective electrodes. However, it should be noted that at least a tenfold amount of Cr(VI) does not interfere with the determination of Cr(III).

Electrodes 1 and 4 were tested as indicator electrodes for the detection of the titration end-point in the determination of chromium by direct titration with EDTA (pH 4.0) and KMnO_4 (pH 3.2).

In determining Cr(III) by direct titration with EDTA, experiments were performed both at room temperature (method 1; Fig. 3, curve 1) and with heating the solutions to 60°C (method 2; Fig. 3, curve 2); fluoride ions were added to the solution [Cr(III) : F = 1 : 1] both at room temperature (method 3; Fig. 3, curve 3) and on heating the solutions to 60°C (method 4; Fig. 3, curve 4). The inflection point in the titration curve obtained by method 1 was indistinct, and the time of attaining a steady-state potential of the chromium-selective electrode was no shorter than 15 min. The electrode potential was unstable. When the solution was heated to 60°C , the rate of complexation between Cr(III) and EDTA increased, and the time the stationary electrode potential was attained decreased to 10 min. The titration end-point was sufficiently clear. The addition of fluoride ions to the solution increased the reactivity of Cr(III); the time the stationary potential of the chromium-selective electrode was attained in this case was reduced to 10 min at room temperature and to 5 min at 60°C .

When chromium-selective electrodes were used to detect the titration end-point in determining Cr(III) in solutions containing $\text{K}_2\text{Cr}_2\text{O}_7$ and fluoride ions [Cr(III) : Cr(VI) : $\text{F}^- = 1 : 1 : 1$], the electrode potential was attained rapidly (for no longer than 5 min) and exhibited the best stability (Fig. 3, curve 5). In the absence of Cr(III) from the solution containing only $\text{K}_2\text{Cr}_2\text{O}_7$, the potential of the chromium-selective electrode remained unchanged on the addition of EDTA. Thus, chromium-selective electrodes based on titanium dichalcogenides intercalated with chromium can be used for determining Cr(III) in the presence of $\text{Cr}_2\text{O}_7^{2-}$, for example, in analyzing slimes in the production of sodium dichromate.

Table 2. Potentiometric selectivity coefficients ($-\log K_{Cr, Me}^{pot}$) of chromium-selective electrodes

Electrode	Na^+	Co^{2+}	Ni^{2+}	Fe^{3+}	Mn^{2+}	$\text{Cr}_2\text{O}_7^{2-}$
$\text{Cr}_{0.1}\text{TiSe}_2$	1	0.1	0.1	0.3	0.2	1
$\text{Cr}_{0.25}\text{TiSe}_2$	1	0.2	0.3	0.2	0.2	2
$\text{Cr}_{0.33}\text{TiSe}_2$	1	1.5	0.4	0.3	0.3	1
$\text{Cr}_{0.25}\text{TiTe}_2$	1	0.3	0.3	0.6	0.3	0.6

A curve of Cr(III) titration with a solution of KMnO_4 is shown in Fig. 4. The titration end-point in this curve can be fixed easily. When determining chromium(III) in solutions containing 0.0330 mmol Cr(III), we found (0.0336 ± 0.0035) mmol Cr(III) ($n = 3$; $P = 0.95$); RSD was no worse than 4%.

To sum up, we should emphasize that chromium-selective electrodes based on the proposed materials cannot be recommended for determining Cr(III) by direct potentiometry, because the pH dependence of the slope of the electrode function is very complex and the electrode is insufficiently selective. At the same time, the electrodes behave well in detecting titration end-points in determining Cr(III) by direct titration with KMnO_4 and EDTA using a potentiometric indication of

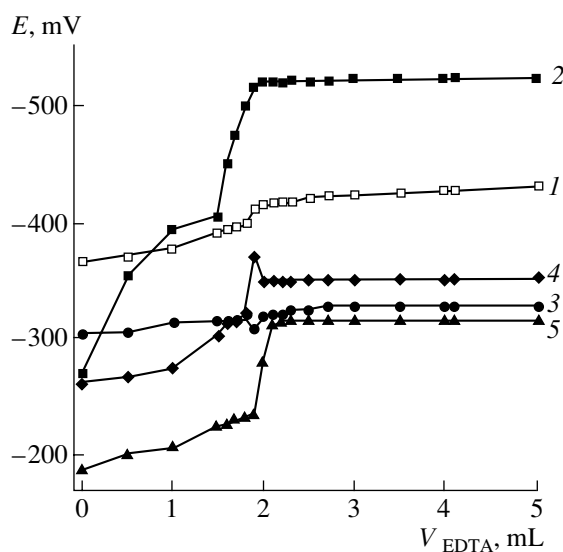


Fig. 3. Curves of potentiometric titration of 0.100 mmol chromium(III) with 0.05 M EDTA at room temperature (method 1, curve 1); on heating to 60°C (method 2, curve 2); in the presence of fluoride ions [Cr(III) : F = 1 : 1] both at room temperature (method 3, curve 3); in the presence of fluoride ions at 60°C (method 4, curve 4); and in the presence of dichromate and fluoride ions [Cr(III) : $\text{Cr}_2\text{O}_7^{2-}$: F = 1 : 1 : 1] at 60°C (method 5, curve 5).

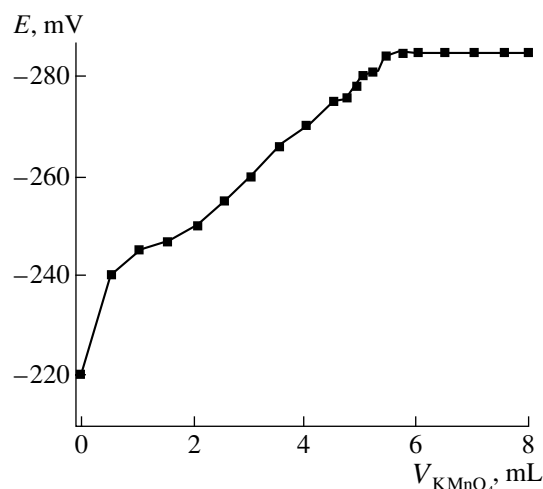


Fig. 4. Curve of potentiometric titration of 0.0590 mmol Cr(III) with a solution of KMnO_4 ($c(1/5\text{KMnO}_4) = 0.0107 \text{ M}$) at pH 3.2.

the titration end-point. Because of the low reactivity of Cr(III), back titration was usually used to determine Cr(III) with EDTA; the titration end-point was detected visually [15]. The use of titanium dichalcogenides intercalated with chromium as active elements of solid-contact chromium-selective electrodes significantly simplifies the experimental procedure for determining Cr(III). To improve the electrode selectivity, it is necessary to optimize the properties of the electroactive material. In this case, the optimization criterion is the width of the linearity range width of the electrode function. Materials with low intercalant concentrations best satisfy the optimization criterion.

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