

Cobalt-Selective Electrode Based on Titanium Ditelluride Intercalated with Cobalt¹

T. V. Velikanova, A. N. Titov, S. G. Mityashina, and O. V. Vdovina

Ural State University, pr. Lenina 51, Yekaterinburg, 620083 Russia

Received December 13, 1999; in final form, March 21, 2000

Abstract—A cobalt-selective solid-contact electrode was prepared on the basis of titanium ditelluride. The electrode exhibits the slope of the electrode function $-(29 \pm 1)$ mV/pC and provides the determination of 1×10^{-5} – 1×10^{-1} M cobalt(II) in the pH range 4.5–6.5. The electrode was used for the potentiometric indication of the titration end point in the determination of cobalt(II) in lanthanum–strontium cobaltite $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$. The intercalant concentration range providing optimal ion-selective properties was determined.

The rapid monitoring of environmental pollution with heavy metals requires reliable, simple, portable, and, preferably, inexpensive monitoring devices. Solid ion-selective electrodes can serve as ideal devices of this type. However, not all of the metals can be determined by this method; e.g., there are no suitable electrodes for the determination of cobalt(II). As reported in the literature, the characteristics of existing electrodes are unsatisfactory [1].

The main requirements to the material for the preparation of the active element of a solid ion-selective electrode are weak bonding between the analyzed ion and the matrix lattice and mixed ion–electron conduction. These conditions are satisfied by intercalation materials, in particular, those based on titanium dichalcogenides. In this work, we examined the possibility of the development of a cobalt-selective electrode based on titanium ditelluride intercalated with cobalt. This material was selected because it exhibits the most covalent bonding among isostructural intercalation compounds [2], which provides the lowest solubility of the material.

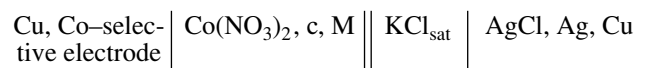
EXPERIMENTAL

As the active element of a solid ion-selective electrode, we used Co_xTiTe_2 obtained by the method of three-stage ampule synthesis from elements. Titanium of iodide purification (99.95% purity), tellurium purified by triple vacuum distillation (at least 99.99% purity), and cobalt (99.9% purity) were used. At the first stage, TiTe_2 was obtained by sintering elements in fused-silica ampules evacuated to 10^{-5} torr at 950°C for 10 days. Next, the content of ampules was removed, triturated, checked for the absence of unreacted titanium, mixed with the corresponding amount of metal

cobalt, pressed to attain good contact between phases, and sintered again in evacuated fused-silica ampules at 800°C for 10 days. Lower sintering temperature compared to the first stage of the synthesis was necessary to prevent the substitution of cobalt atoms for titanium in the matrix lattice, as it was observed for iron intercalates [3]. Usually, we failed to attain homogeneity of the sintered material under these synthesis conditions. Therefore, after the second stage of the synthesis, the material was again triturated, pressed, and homogenized by annealing under the same conditions. The resulting material was homogenous within the accuracy of X-ray diffraction analysis (DRON-3M diffractometer, $\text{Cu } K_\alpha$ radiation, graphite monochromator). The conductivity was measured by the standard four-probe method; it was 100–500 S/cm depending on the concentration of intercalated cobalt. Ion conductivity was estimated by the Nernst–Einstein equation using times required for attaining homogeneity on annealing; it was 10^{-6} – 10^{-9} S/cm. Thus, the contribution of ion conductivity to total conductivity is insignificant.

For measurements, we used a film active element prepared by applying a mixture of Co_xTiTe_2 with a solution of polystyrene in methyl ethyl ketone onto a current lead and drying; the current lead was obtained by filling the end of a glass tube with Wood alloy. The procedure for preparing electrodes is described in detail in [4].

Electrode characteristics of Co-selective electrodes were studied by the measurement of the electromotive force in the circuit



using EV-74 and I-115 instruments in the millivoltmeter mode; pH of solutions was monitored with a glass electrode using a pH-673 instrument. All measurements were performed at $20 \pm 2^\circ\text{C}$. Before measurements, electrodes were washed with distilled water

¹Presented at the V All-Russian Conference with the Participation of CIS Countries on Electrochemical Methods of Analysis (EMA-99), Moscow, December 6–8, 1999.

acidified to a particular pH with closed electric circuit until constant potential was attained. If after long-term operation electrodes changed their electroanalytical characteristics, they were conditioned in 10^{-3} M $\text{Co}(\text{NO}_3)_2$ or CoSO_4 for 30 min with closed circuit with subsequent washing in distilled water for 20 min until constant potential was attained. Between measurements, electrodes were kept dry.

The dependence of the potential of Co-selective electrodes on the concentration of Co(II) was studied in 1×10^{-6} – 1×10^{-1} M solutions of $\text{Co}(\text{NO}_3)_2$ or CoSO_4 at constant pH in the range 1.0–6.5. The selectivity of electrodes was assessed by the mixed solution method ($c_{\text{Me}} = 5 \times 10^{-3}$ M). For the titrimetric determination of cobalt, we used 0.05 M EDTA (pH 5.0, acetate buffer solution) or KMnO_4 ($c(1/3\text{KMnO}_4) = 0.006$ M, pH 6.0) as titrants. The titration end point was determined graphically from the integral (E (mV) vs. V (mL)) and differential (dE/dV vs. V (mL)) titration curves and by the Gran method. From the obtained data, a calibration plot was constructed on the coordinates amount of the titrant (mmol) vs. amount of cobalt (mmol).

RESULTS AND DISCUSSION

As demonstrated in [2], cobalt atoms intercalated into TiTe_2 form covalent sites Ti–Co–Ti. Evidently, ion-selective properties of the Co_xTiTe_2 material can depend on the concentration of these sites. At low concentrations of the intercalant, the sites can be considered as isolated, which hinders electron transfer between sites and provides pronounced covalent character of bonding between the intercalant and the matrix lattice. At high concentrations, overlapping of hybrid states of neighboring sites must lead to band broadening and impart partially metallic character to the bond between cobalt and the matrix lattice. Thus, the best ion-selective properties are expected for materials with a low concentration of the intercalant. On the other hand, it is not inconceivable that these materials contain unintercalated regions, which can unselectively dissolve many metals. The composition $\text{Co}_{0.25}\text{TiTe}_2$ can be considered the transition point from low to high con-

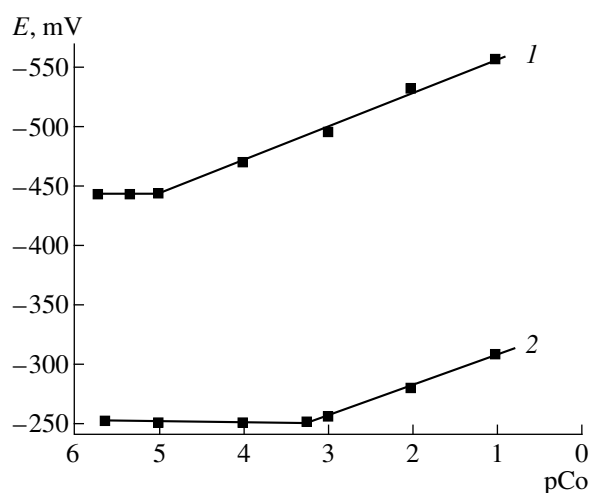


Fig. 1. Electrode functions of Co-selective electrodes based on Co_xTiTe_2 : (1) $\text{Co}_{0.25}\text{TiTe}_2$ (electrode 1), (2) $\text{Co}_{0.4}\text{TiTe}_2$ (electrode 2), pH 5.5.

centrations; this concentration of the intercalant corresponds to the percolation threshold by the Ti–Co–Ti sites in the hexagonal lattice with bonds only between nearest neighbors [2]. Therefore, in this work we studied ion-selective properties of $\text{Co}_{0.4}\text{TiTe}_2$ (material with the concentration of intercalant higher than the percolation threshold) and $\text{Co}_{0.25}\text{TiTe}_2$ (material whose ion-selective properties must be optimal in view of above reasoning).

Electrode characteristics of Co-selective electrodes based on $\text{Co}_{0.25}\text{TiTe}_2$ (electrode 1) and $\text{Co}_{0.4}\text{TiTe}_2$ (electrode 2) in $\text{Co}(\text{NO}_3)_2$ solutions are presented in Table 1, and the corresponding linear portions of electrode functions are shown in Fig. 1. From these results, it follows that electrode 1 based on $\text{Co}_{0.25}\text{TiTe}_2$ exhibits the best electrode characteristics. The electrode function of a Co-selective electrode based on this material is linear in the cobalt concentration range 1×10^{-5} – 1×10^{-1} M and exhibits the anionic character. According to [5], hybrid states of the intercalant and the matrix lattice that occur because of the intercalation of titanium dichalcogenides with transition metals lie below the Fermi level

Table 1. Electrode characteristics of cobalt-selective electrodes

Electrode	Electrode-active compound	Test solution	Linearity range of the function $E = f(\text{p}c_{\text{Co}})$, M	Slope of the electrode function, mV/pc	Working pH range
1/ $\text{Co}_{0.25}\text{TiTe}_2$		CoSO_4 , pH 5.5	1×10^{-5} – 1×10^{-1}	–(29 ± 1)	4.5–6.5
1/ $\text{Co}_{0.25}\text{TiTe}_2$		$\text{Co}(\text{NO}_3)_2$, pH 5.5	1×10^{-5} – 1×10^{-1}	–(30 ± 2)	4.5–6.5
2/ $\text{Co}_{0.4}\text{TiTe}_2$		CoSO_4 , pH 5.5	1×10^{-3} – 1×10^{-1}	–(22 ± 2)	4.5–6.5
2/ $\text{Co}_{0.4}\text{TiTe}_2$		$\text{Co}(\text{NO}_3)_2$, pH 5.5	1×10^{-3} – 1×10^{-1}	–(26 ± 1)	4.5–6.5

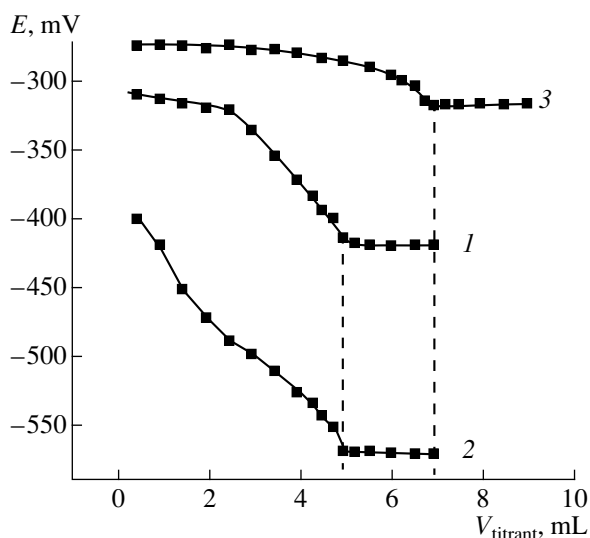


Fig. 2. Curves of the potentiometric titration of Co(II); (1, 2) $c_{\text{Co}} = 0.03$ mM, titrant KMnO_4 ($c(1/3\text{KMnO}_4) = 0.006$ M), pH 6.0; (1) CoSO_4 solution; (2) model mixture Co : La : Sr = 1 : 1 : 1; (3) $c_{\text{Co}} = 0.35$ mM, titrant 0.05 M EDTA, pH 5.0.

of the initial material. These states must exhibit electron-withdrawing properties like the states of oxidant atoms. This fact explains the anionic character of the electrode function, i.e., the shift of the electrode potential to the negative region upon increasing the concentration of cobalt in the test solution. The detection limit of cobalt(II) in pure solutions for this electrode was 4×10^{-6} M. The slope of the electrode function is the closest to the theoretical value for a doubly charged ion in the pH range 4.5–6.5 (-29 ± 1 mV/pc). The characteristics of electrodes 1 and 2 in $\text{Co}(\text{NO}_3)_2$ and CoSO_4 solutions are nearly the same, i.e., the nature of the anion has no effect.

The response time t_{90} on switching from water to 1×10^{-6} – 1×10^{-5} M solutions is 3–2.5 min and less than 1 min for concentrations above 1×10^{-4} M both in

Table 2. Potentiometric selectivity coefficients ($-\log K_{\text{Co}, \text{M}}^{\text{pot}}$) for cobalt-selective electrodes

Ion	Electrode 1	Electrode 2
La^{3+}	0.7	0.7
Ni^{2+}	1	1
Sr^{2+}	1	2
Mn^{2+}	1	1
Pb^{2+}	2	2
Fe^{3+}	1	2

sulfate and nitrate solutions; the complete equilibration time t_{100} is 10–9 min and 7–3 min, respectively. The potential drift was no larger than ± 1 mV in a day; the detection limit of cobalt remained constant within this time. On prolonged operation, the electrode potential is shifted to the positive region with the rate about 10 mV per month. The service life of the electrode is at least 400 h of continuous operation. During our studies (more than 15 months), the electrode retained its characteristics on keeping dry between measurements.

Table 2 presents potentiometric selectivity coefficients determined by the mixed solution method ($c_{\text{Me}} = 5 \times 10^{-3}$ M). The determination of Co(II) is not affected by the interference from fivefold amounts of La(III) and tenfold amounts of Ni(II) and Mn(II) for electrodes 1 and 2; tenfold amounts of Sr(II) and Fe(III) for electrode 1; and hundredfold amounts of Sr(II) and Fe(III) for electrode 2.

Electrode 1 was used for the indication of the end point in the chelatometric and permanganometric titration of cobalt(II). The titration curve of cobalt(II) with 0.05 M EDTA in an acetate buffer solution at pH 5.0 (Fig. 2, curve 3) indicated that the titration end point in the integral curve is determined rather clearly. Processing of titration curves by three different methods (integral, differential, and Gran) gave identical results. It was found that the titration of cobalt(II) with EDTA is affected by the interference from La(III) and Sr(II). For improving the selectivity of the titrimetric determination of cobalt(II) using electrode 1, we used KMnO_4 ($c(1/3\text{KMnO}_4) = 0.006$ M, pH 6.0) as the titrant [6]. Results of the titration of cobalt(II) with a solution of KMnO_4 in pure solutions (Fig. 2, curve 1) and in a model mixture containing Co : La : Sr = 1 : 1 : 1 (Fig. 2, curve 2) indicate that cobalt(II) can be selectively determined in the presence of lanthanum(III) and strontium(II).

In the permanganometric determination of cobalt(II) in a sample of lanthanum–strontium cobaltite $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ containing 26.76% cobalt, $26.52 \pm 0.53\%$ Co was found ($n = 5$, $P = 0.95$). The relative standard deviation was 1%. The accuracy of the results was confirmed by the standard addition method and by the independent method (indirect complexometric determination of cobalt using a fluoride-selective electrode for the potentiometric indication of the titration end point in the presence of indicator amounts of fluoride ions).

Thus, titanium ditelluride intercalated with cobalt at intercalant concentrations corresponding to the percolation threshold by the covalent sites ($\text{Co}_{0.25}\text{TiTe}_2$) can be recommended as the electrode-active compound for Co-selective electrodes that provide the determination of cobalt(II) in complex samples.

ACKNOWLEDGMENTS

The work was supported by the Russian Foundation for Basic Research, project no. 98-03-32538a and partially supported by the US Civilian Research and Development Foundation for the Independent States of the Former Soviet Union (CRDF), Award no. REC-005.

REFERENCES

1. Demina, L.A., Krasnova, N.B., Yurishcheva, B.S., and Chupakhin, M.S., *Ionometriya v neorganicheskom analize* (Potentiometry with Ion-Selective Electrodes in Inorganic Analysis), Moscow: Khimiya, 1991.
2. Titov, A., Titova, S., Neumann, M., Pleschov, V., Yarmoshenko, Yu., Krasavin, L., Dolgoshein, A., and Kuranov, A., *Mol. Cryst. Liq. Cryst.*, 1998, vol. 311, p. 161.
3. Calvarin, G., Gavarrri, J.R., Buhannic, M.A., Colombet, P., and Danot, M., *Rev. Phys. Appl.*, 1987, vol. 22, no. 10, p. 1131.
4. Velikanova, T.V., Titov, A.N., and Shishmintseva, N.N., *Zh. Anal. Khim.*, 2000, vol. 55, no. 11, p. 1172.
5. Titov, A.N. and Dolgoshein, A.V., *Fiz. Tverd. Tela* (Leningrad), 2000, vol. 42, no 3, p. 425.
6. Aleksandrov, G.P., Shuter, Ya.N., and Shevchenko, Yu.V., *Ukr. Khim. Zh.*, 1962, vol. 28, no. 7, p. 871.