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Solid-contact ionophore-based electrode for determination of pH in acidic media

Elisaveta N. Samsonova · Viktor M. Lutov ·
Konstantin N. Mikhelson

Abstract Solid-contact electrode for pH measurements in acidic media is described. The sensor membrane is made of polyvinyl chloride plasticized with bis(2-ethylhexyl)phthalate and contains neutral pH-selective ionophore hexabutyltriamidophosphate and potassium tetrakis-p-Cl-phenylborate cation exchanger. The transducer layer of the solid-contact electrode contains the same membrane composition and also carbon black and electron–ion-exchanger resin EI-21(a cation exchange resin containing fine dispersion of metal copper) for stabilization of the electrode potential. The electrode is suitable for measurements of pH in the range 0–6 and works also in hydrofluoric acid (HF) solutions up to 0.1 M HF. Chronopotentiometric measurements show diffusion-limited polarization at the interface between sensor membrane and transducer layer. The slope of the linearized polarization curve correlates with the long-term stability of the electrode potentials providing a tool for prediction of the long-term stability of solid-contact potentiometric sensors.

Keywords Solid-contact electrode · Neutral ionophore · pH measurements · Long-term stability

Introduction

Control of pH belongs to the most frequently performed measurements, and silicate glass pH electrode including solid-contact electrode [1] remains predominating among other sensors for measurements of pH. Unfortunately, silicate glass membranes possess some disadvantages. In particular, these membranes do not stand fluoride solutions. Therefore ion-selective electrodes (ISEs) with polymeric membranes and especially solid-contact pH ISEs may comprise a good alternative to glass electrodes.

Highly selective pH electrodes with polyvinyl chloride (PVC) membranes are known since 1980s [2–5]. More recently, other ionophore-based pH electrodes have been described [6–13]. In most cases, the ionophores in these pH-selective electrodes were of amine nature with few exceptions, like electrode based on octadecyl isonicotinate ionophore suitable for gastric applications [4, 13].

Measurements of pH in the presence of fluoride are challenging primarily in acidic media, in various industrial samples. High affinity of amine ionophores to hydrogen ions results in high coextraction of electrolytes (acids) into such membranes. Therefore, the reported working pH range of ISEs with lipophilic amines as ionophores is typically pH 4–10.

Earlier, we have reported on a pH-selective electrode based on neutral ionophore hexabutyltriamodophosphate (HBTAP), which is suitable for pH measurements in the range pH 0 through 6, and works in hydrofluoric acid (HF) solutions up to 0.1 M [7, 14]. It was shown by segmented sandwich membrane method that the ionophore forms complex HL_2^+ with stability constant $\log \beta \approx 9.3$. Peculiar stoichiometry of the complex suggesting divalent hydrogen was attributed to complexation of H_3O^+ hydroxonium ion (rather than just H^+) via hydrogen bonds as shown in Fig. 1a [14].

Stabilization of the potential of a solid-contact electrode requires a layer with mixed ionic and electronic conductivity in between sensor membrane (ionic conductor) and electronically conducting substrate. Among the first materi-

E. N. Samsonova · V. M. Lutov · K. N. Mikhelson (✉)
Chemistry Institute, St. Petersburg State University,
26 Universiteskij Pr., Stary Peterhof,
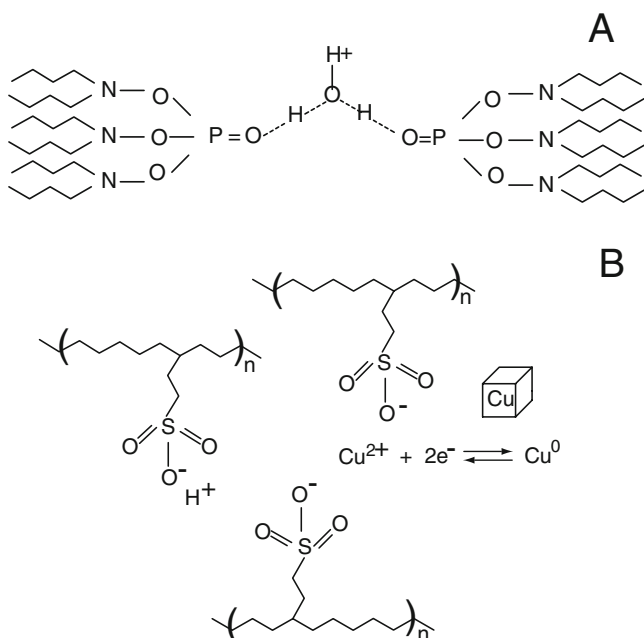198504 St. Petersburg, Russia
e-mail: konst@km3241.spb.edu

Fig. 1 Structures of HBTAP complex with hydrogen (**a**) and of EI-21 electron–ion exchange resin (**b**)

als for this intermediate layer was a chinone–hydrochinone electron–ion-exchange resin EO-7 utilized in pioneering work [15]. Later on, electron–ion-exchange resin EI-21 with Cu^0/Cu^{2+} redox couple (see Fig. 1b) was used for stabilization of a number of solid-contact ISEs [16–18]. Basically, EI-21 is a cation exchange resin. Tiny particles of metal copper appear in the resin after partial reduction of EI-21 in Cu^{2+} form. The presence of some EI-21 in H^+ form prevents from hydrolysis of Cu^{2+} to $CuOH^+$ to $Cu(OH)_2$.

Nowadays, conducting polymers are most frequently used as ion-to-electron transducers in solid-contact ISEs [19–30]. Recently, we found that combination of conducting polymer poly(aniline) with electron–ion-exchange resin EI-21 in transducer layer of a nitrate-selective solid-contact electrode is advantageous for long-term stability of potentials [31].

In this paper, we report on solid-contact pH electrode based on HBTAP as neutral ionophore with electron–ion-exchanger resin EI-21 in the transducer layer. For this electrode, it is shown that long-term stability of the potentials correlates with diffusion polarization in the vicinity of the interface between ionic conductor (membrane layer) and ion-to-electron transducer layer.

Materials and methods

Neutral ionophore HBTAP has been synthesized in Chemical Faculty of St. Petersburg University by Dr. S.V. Nikolaev in accordance with [7]. Other membrane compo-

nents poly(vinyl chloride) high molecular weight (PVC), bis(2-ethylhexyl)phthalate (DOP), and potassium tetrakis(p-Cl-phenyl)borate (KClTPB) were Selectophore-grade reagents from Fluka (Buchs, Switzerland). Tetrahydrofuran (THF) and cyclohexanone (CH) were from Vecton (St. Petersburg, Russia). Electron–ion-exchanger resin EI-21 was obtained from Prof. T.A. Kravchenko (Voronezh State University, Voronezh, Russia). Carbon black P-3679 (CB) and inorganic salts and acids were from Reachim (Moscow, Russia). Aqueous solutions were prepared with bidistilled water.

Membrane cocktails were prepared by dissolving suitable amounts of PVC, DOP, HBTAP, and KClTPB in THF. Membranes of solid-contact electrodes contained three layers: (a) with pure ionic conductivity, (b) with mixed electronic–ionic conductivity, and (c) with electronic conductivity. Layer (a) was ordinary membrane layer consisting of PVC, DOP, HBTAP, and KClTPB. The PVC to DOP mass ratio was 1:3, and the concentrations of HBTAP and KClTPB in DOP were 0.1 and 0.01 M respectively. This particular formulation was found optimal for pH-sensing properties of the electrode in our earlier studies [7, 14]. Layer (b) consisted of PVC, DOP, carbon black, and EI-21. The mass ratio of these components was 1:3:1:0.3, as it was recommended earlier [16–18]. The resin was either in Cu^{2+} form, or in H^+ form, or in mixed form. Layer (c) contained PVC and DOP and also carbon black in the mass ratio 1:1:1. We emphasize here that DOP in layers (b) and (c) contained HBTAP and KClTPB in the same concentrations as in layer (a). In this way, we tried to avoid diffusion of HBTAP and KClTPB from layer (a) to layer (b) to (c) and the respective changes of the potential over time.

Electrode membranes were prepared by drop casting the layers on glass Petri dishes, one layer on the top of the other. Layer (a) was casted first. After evaporation of THF from layer (a), layer (b) was casted on the surface of layer (a), and then layer (c) was casted on the surface of layer (b). Layer (a) is colorless and transparent; layer (b) is dark brown because of the combination of EI-21 (brown) and CB (black), and layer (c) is black because of high content of carbon black. Crosscutting membranes revealed sharp interfaces between the layers indicated by these colors. However, some mixing between the layers is possible regarding PVC and DOP (EI-21 and carbon black do not dissolve in THF). Therefore, the ratio of PVC to DOP in the vicinity of the interface between layers (b) and (c), most probably, changes gradually from 1:3 in (b) to 1:1 in (c). Because this ratio in layers (a) and (b) is the same, mixing between these layers seems irrelevant.

Solid-contact electrodes were prepared by cutting discs with diameter of 6 mm and fixing them in PVC bodies with PVC dissolved in CH. Contact wires were glued to back (c) sides of the membranes using cocktail (c) as glue, see Fig. 2.
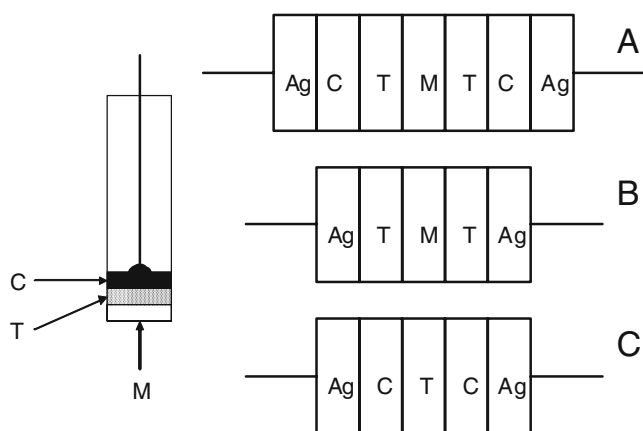
Fig. 2 Electrode design (*left*) and symmetric sandwiches for chronopotentiometric measurements (*right*). Ag—silver plate, C—carbon black composite layer, T—transducer layer, M—membrane layer

For chronopotentiometric measurements, the layers of all tree kinds were prepared separately, and then three-layer or five-layer sandwiches (see Fig. 2) were assembled and fixed with clamps.

Potentiometric measurements were performed with pH/mV-meter pX-150 (Izmeritel, Gomel, Belarus). The reference electrode was Ag/AgCl in 3.5 M KCl, and the salt bridge was filled with 3.5 M KCl.

The solutions were either buffered or not buffered (HCl, HNO$_3$, H$_2$SO$_4$, and HF). The buffer solutions were the tartaric acid buffer with pH 3.56 and a series of acetic acid buffer solutions with pH from 2 to 5. The actual values of the pH in HCl, HNO$_3$, and H$_2$SO$_4$ were measured with glass pH electrode ESL-43-07 (Izmeritel, Gomel, Belarus). In the case of HF, use of glass electrode was not possible. On the other hand, because of significant association of HF, these solutions are buffered by themselves. Therefore the actual pH in HF solutions was calculated by iteration procedure using $\log K = -3.20$ for HF dissociation constant [32]. To be sure about the reliability of these calculations, we calculated activity of H$^+$ and also that of F$^-$, and then compared the mean electrolyte activity of HF $a_{\pm HF} = \sqrt{a_H a_F}$ with the respective values tabulated in [32]. The difference between calculated and tabulated values never exceeded 5%, so the iteration procedure did produce reliable data upon activities of both ions: H$^+$ and F$^-$.

The measured EMF values were corrected for liquid junction potentials using Henderson formalism.

Chronopotentiometric measurements were performed with potentiostat–galvanostat Autolab 30 (Ecochemie, The Netherlands). These experiments were done with three-layer or five-layer sandwiches including layers with ionic, electronic, and mixed conductivity but without aqueous solution. In this way, any polarization effects which may be possible on the membrane–solution interface were eliminated, and the registered polarization referred solely to these layers and interfaces between the layers. The measurements were performed in two-electrode setup so that one of silver plate electrodes was the working electrode and the other was the reference and counter electrode.

All measurements were performed at room temperature: 21±2 °C.

Results

Solid-contact electrodes with six different compositions of the ion-to-electron transducer layer were studied together with a conventional electrode with internal aqueous solution. The compositions of the transducer layer are summarized in Table 1.

The pH response of the electrodes was characterized by calibrations in pH-buffered solutions and also in HCl, HNO$_3$, H$_2$SO$_4$, and HF solutions. The experimental results for all the electrodes obtained in buffer solutions and in HCl, together with theoretical Nernstian response line (the slope 58 mV/pH) are presented in Fig. 3. One can see that within the range pH 0–7 all the electrodes provide near-Nernstian response. The slope values are given in Table 2.

In H$_2$SO$_4$ solutions, the electrodes showed Nernstian slope up to pH 0—the same as in HCl. However, in HNO$_3$, the upper limit of linear response was pH 1, and the slope gradually became anionic in more concentrated acid. Analogous behavior was registered in HF solutions. All the electrodes provided near-Nernstian response up to pH 2.3 which corresponds to 0.1 M HF and showed anionic slope at pH 1.5–2.

These results are consistent with our previous findings with conventional pH ISEs based on HBTAP [14]. The sequence of the anion interference was therefore as follows:

$$F^- > NO_3^- > Cl^- \approx SO_4^{2-}$$
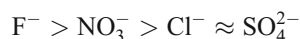
Apparently, non-Hofmeister position of F$^-$ in this sequence can be attributed to coextraction of neutral HF ion pairs from solution into the membrane which is stronger than coextraction of charged ions.

For characterization of the selectivity, K$^+$, Na$^+$, and Cu^{2+} ions were chosen as suitable representatives. The choice of Na$^+$ and K$^+$ ions for the selectivity characterization was mostly because of the abundance of these ions in various practically relevant samples. Copper ion interference had to be studied primarily because of the presence of Cu^{2+} in the ion-to-electron transducer layer and also because the electrode was intend for use in copper plating process.

It could be useful to measure the unbiased selectivity coefficients in accordance with the protocol invented in [33, 34]. However, in the case of pH electrodes, it would require

Table 1 The compositions of the ion-to-electron transducer layer

Electrode	DOP + ionophores (g)	EI-21 Cu^{2+} (g)	EI-21 H$^+$ (g)	PVC (g)	Carbon black (g)
1	1.50	0.030	0.000	0.50	0.50
2	1.50	0.027	0.003	0.50	0.50
3	1.50	0.020	0.010	0.50	0.50
4	1.50	0.015	0.015	0.50	0.50
5	1.50	0.000	0.030	0.50	0.50
6[a]	1.50	0.000	0.000	0.50	0.50
7[b]	1.50	0.000	0.000	0.50	0.00

[a] Coated-wire-type electrode with direct contact between membrane and carbon black composite

[b] Conventional electrode filled with tartaric acid buffer pH 3.56 with 0.01 KCl background

initial soaking in alkaline solutions which would damage the membranes because of the hydrolysis of the plasticizer (DOP). Therefore, the selectivity of the electrodes to H$^+$ over Na$^+$, K$^+$, and Cu^{2+} was studied by measurements in HCl solutions with 1 M KCl or NaCl, or 0.1 M CuCl$_2$ background. The pH values in the bulk of the solution were measured with glass pH electrode. Obviously, these values were not necessarily the same as in the vicinity of the electrode membranes, and some contamination of solutions with H$^+$ ions released by the membranes was inevitable. Therefore, the data on the selectivity which are summarized in Table 2 may differ from the unbiased values and must be considered as apparent.

The selectivity of solid-contact ISEs was virtually independent on the composition of the transducer layer. However, the selectivity of the conventional electrode was in 0.4–0.7 logarithmic unit worse. Most probably, solid-contact ISEs contaminate the samples with H$^+$ ions in lesser extent than the conventional electrode filled with pH buffer.

We will turn now to the issue which is especially important for solid-contact ISEs: the long-term stability of
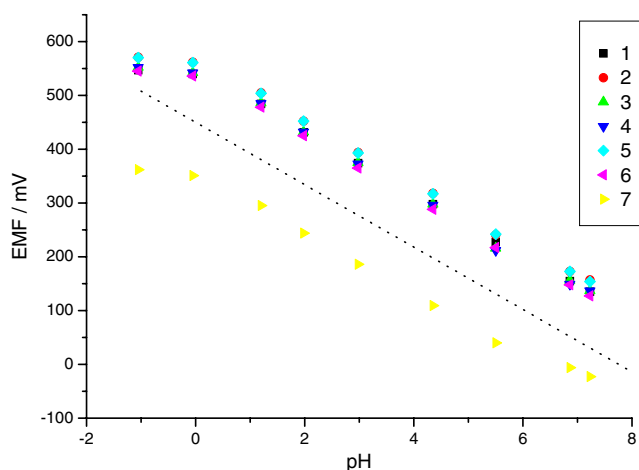

Fig. 3 The pH response of solid-contact and conventional pH electrodes based on HBTAP in pH buffers and in HCl. The *numbers* in the legend correspond to the electrode numbers in Table 1. Each experimental point is averaged from three replica electrode

the potentials in a given solution. The respective measurements were performed in tartaric acid buffer solution with pH 3.56 over 38 days.

The potential of conventional electrode was remarkably stable over time, at the level of 138±1 mV in the tartaric acid buffer. The record of the potential stability of solid-contact electrodes is presented in Fig. 4. One can see that initially the potentials of all the solid-contact electrodes were drifting during about 10 days from more positive to less positive values. This drift can be attributed to slow uptake of water, and it was shown that conditioning in solutions at 60 °C allows for shortening the time of this drift [15–17].

After that, the potentials of the electrodes with the electron–ion-exchanger EI-21 in the transducer layer became relatively stable. However, the potentials of electrodes with the direct contact of the PVC membrane with carbon black composite (electrode 6) which is analogous to coated-wire electrode remained drifting.

These results are typical for solid-contact electrodes: the presence of a transducer layer allows for remarkably higher stability than in the case of the so-called coated-wire electrodes. However, the potentials are still not as stable as those exhibited by conventional electrodes. Unlike in the case of conventional ISEs, the particular values of the solid-contact electrode potentials cannot be easily traced to known standard potential values. Also, these values varied from one replica electrode to another. In this research, the piece-to-piece variation of the potentials was from ±3 mV for electrodes with the transducer layer composition 2 to ±15 mV for coated-wire-type electrodes 6.

All in all, solid-contact electrode 2 provided the best stability over time among other solid-contact electrodes studied here, and coated-wire-type electrode 6 was the worse. This is consistent with earlier findings related to various solid-contact ISEs with electron–ion-exchanger EI-21 in transducer layer. It was found earlier that the optimal ratio of the Cu^{2+} form of the resin over the H$^+$ form is 10:1 [16–18]. The role of the resin in the transducer layer is of course providing with a redox couple which in this case is

Table 2 Sensor properties of the electrodes

Electrode	Slope (mV/pH)	$\log K_{H/K}$	$\log K_{H/Na}$	$\log K_{H/Cu}$
1	56.8±0.9	−6.5±0.2	−6.4±0.3	−5.0±0.5
2	57.7±1.0	−6.3±0.2	−6.3±0.4	−5.0±0.4
3	57.7±1.4	−6.3±0.3	−6.4±0.3	−4.8±0.4
4	58.7±1.3	−6.5±0.3	−6.4±0.3	−5.0±0.5
5	57.4±0.9	−6.5±0.2	−6.2±0.3	−4.8±0.4
6	57.5±0.9	−6.4±0.2	−6.3±0.4	−4.8±0.4
7	56.8±1.0	−5.9±0.2	−5.7±0.2	−4.4±0.3

Cu^{2+}/Cu^{0}. Carbon black ensures electronic conductivity through the whole transducer layer and also high electric capacitance which is beneficial for the long-term stability of solid-contact electrodes [21].

It would be interesting to trace the long-term stability to some other property of a solid-contact electrode which can be measured fast. Then one would be able to foresee whether the particular solid-contact ISE is promising in terms of long-term stability of readings.

Earlier [22, 23, 31], we tried to find a correlation between the long-term stability and the impedance parameters of solid-contact electrodes. The idea was that insufficient stability and piece-to-piece reproducibility come from slow redox reaction in the transducer layer, so that the transduction from ionic to electronic conductivity is partially blocked. Surprisingly, the recorded impedance spectra did not suggest any blocked interface. Basically, only membrane layer resistance and the respective geometric capacitance appeared in the spectra.

In this research, we decided to concentrate on possible, relatively slow processes which may cause the insufficient stability of the potentials of solid-contact ISEs. These processes could be slow transportation of species produced or consumed in the course of redox reaction in the

transducer layer. In principal, slow transportation can be detected and quantified by measuring impedance at low frequencies. However, chronopotentiometry (as well as chronoamperometry) seems intuitively clearer and more convenient for this kind of research. In this work, we used therefore galvanic pulse method (chronopotentiometry).

The measurements were performed with symmetric sandwiches containing ordinary clear PVC membrane layer (a) in the center, with transducer layers (b) and layers with electronic conductivity (c) on both sides of the clear layer. The contact pads were made of copper discs with electrochemically deposited silver. The sandwiches are shown schematically in Fig. 2 (A–C). The symmetry of the sandwiches allows for calculation of the interfacial polarization at each of the sides of the clear membrane layer from the total measured effect.

The sandwiches were polarized with current steps with current density in the range 2×10^{-9} to 8×10^{-9} A/cm^2; it was assumed that electrochemically active surface area equals the visible area which was 1.54 cm^2. The signals were recorded in the time range from 10 μs to 100 s.

Measurements with three-layer C-type sandwiches (see Fig. 2) showed that currents within $1 \times 10^{-9} – 1 \times 10^{-8}$ A/cm^2 did not cause polarization of the interfaces between silver plates and carbon black composite, neither between carbon black composite and transducer layer with EI-21, confirming the suitability of two-electrode setup for our experiments. In addition to this, the comparison of the results obtained with five-layer (A-type) and with three-layer (B-type) sandwiches showed that in both setups the results were the same. Obviously, Ohmic resistance of the membrane layer as well as polarization between the membrane layer and transducer layer predominate over other effects. Therefore, all further measurements were performed with three-layer sandwiches of type B.

For comparison, analogous measurements have been done also with conventional electrode, in symmetric conditions. The membrane was placed in between two aqueous solutions of the same composition: tartaric acid buffer with pH 3.56 with 0.01 M KCl background. The internal Ag/AgCl electrode was used as working electrode, and Ag/AgCl in the external solution was the reference and counter electrode.
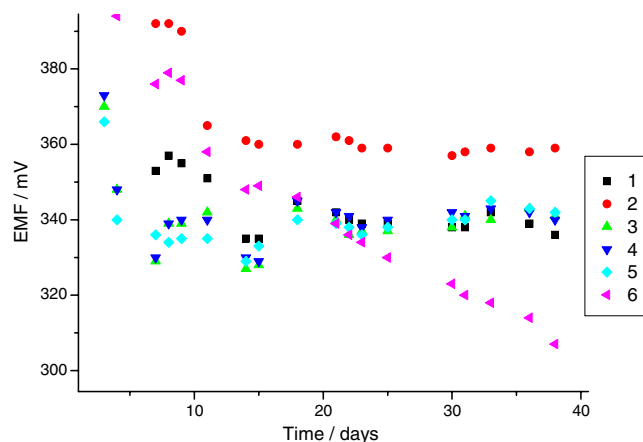

Fig. 4 Potentials of the solid-contact ISEs in tartaric acid buffer solution over time. The *numbers* in the legend correspond to electrode numbers in Table 1. Each experimental point is averaged from three replica electrode
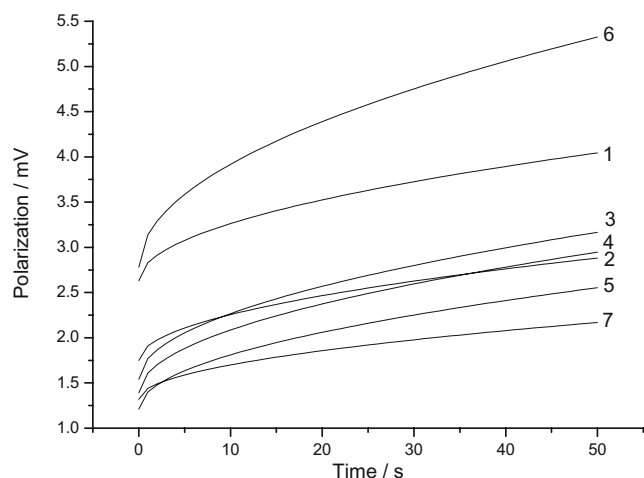
Fig. 5 Original chronopotentiometric curves obtained with B-type three-layer sandwiches polarized with current density of 4×10^{-9} A/cm^2. The *numbers* in the legend correspond to electrode numbers in Table 1

The chronopotentiometric curves η polarization vs. t time obtained with current density of 4×10^{-9} A/cm^2 are presented in Fig. 5. It can be seen (Fig. 6) that the original curves became straight lines when plotted against square root of time, suggesting the process is limited by diffusion.

The results of chronopotentiometric studies together with the scattering of the electromotive force of the respective solid-contact electrodes after the first 10 days in solution are summarized in Table 3. One can see that the slopes of linearized chronopotentiometric curves correlate with the long-term stability of the electrode potentials. Indeed, the value of $d\eta/d\sqrt{t}$ obtained for electrode 2 (the most stable among the solid-contact electrodes studied) is the lowest, and $d\eta/d\sqrt{t}$ for the coated-wire-type electrode 6 is the highest. The correlation between $d\eta/d\sqrt{t}$ values and long-term stability of the ISEs is presented in Fig. 7.
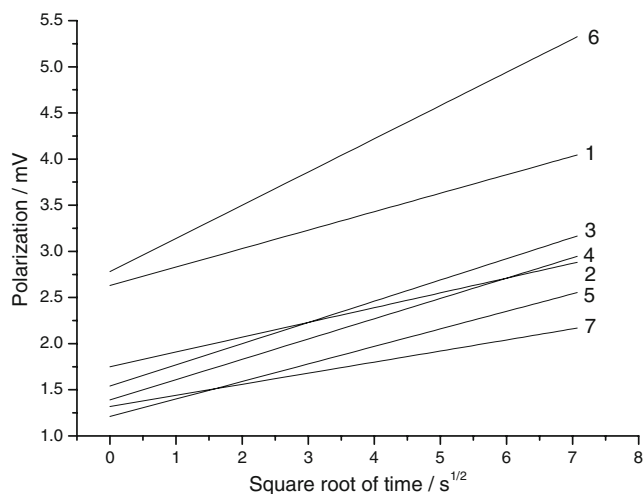

Fig. 6 Linearized chronopotentiometric curves obtained with B-type three-layer sandwiches. The *numbers* in the legend correspond to electrode numbers in Table 1

Table 3 Polarization results and EMF scattering

Number	H$^+$ to Cu^{2+}	$d\eta/d\sqrt{t}$ (mV/s$^{1/2}$)	EMF scattering (±mV)
1	0:1	2.0	4.4
2	0.1:1	1.6	2.1
3	0.3:1	2.3	5.2
4	1:1	2.2	4.7
5	1:0	1.9	4.3
6	0:0	3.6	15.5
7	Conventional electrode	1.2	1.1

Although the correlation does exist (the correlation coefficient is 0.987), the variation of the $d\eta/d\sqrt{t}$ values is small so this criterion is not very sensitive. Also, the point related to the conventional electrode is not far from the correlation line. When this point is included into the linear fit, the correlation coefficient reduces only a little bit: to 0.977.

Chronopotentiometry was used earlier [21] to compare a coated-wire-type K$^+$ ISE with a glassy carbon substrate and a same kind of electrode with solid contact stabilized with poly(3,4-ethylenedioxythiophene)–poly(4-styrenesulfonate) system (PEDOT–PSS). It was found that passing current of 1 nA causes polarization of a coated-wire electrode of about 70 mV over 60 s, while polarization of the ISE with PEDOT–PSS was negligible. Impedance measurements revealed large charge transfer resistance at the interface between glassy carbon and PVC membrane in the coated-wire-type electrode, while in the case of the solid-contact ISE with PEDOT–PSS only membrane bulk semicircle was registered [21].
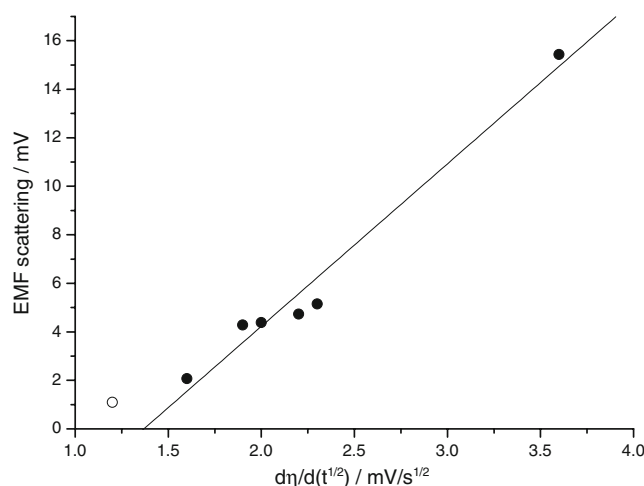

Fig. 7 Correlation between the slope of linearized chronopotentiometric curve and the scattering of the EMF in the control solution. *Filled symbols* refer to solid-contact electrodes with different compositions of the transducer layer (electrodes 1–6). *Open symbol* refers to conventional electrode 7

In our case, unlike in [21], the registered polarization was of diffusion nature, for all kind of electrodes. Also, even coated-wire-type electrode 6 showed relatively small polarization, noncomparable with that reported in [21]. This difference may be caused by large contact area of carbon black dispersion, so the charge transfer resistance was much smaller and the capacitance was much larger than in the case of polished glassy carbon substrate.

The polarization is dependent on the ratio of the content of EI-21 resin in the Cu^{2+} form over that in the H^+ form. Therefore, the registered effects are somehow related to the diffusion of Cu^{2+} and H^+ ions in the vicinity of the resin particles. However, it is not yet clear why certain ratio between the resin in the H^+ form and in the Cu^{2+} form is more beneficial for low polarization and better stability of potentials than some other ratio. It should be also noted that the polarization of conventional electrode although lower than that of the best solid-contact ISE was of the same order of magnitude. This is somewhat surprising bearing in mind significantly better stability and piece-to-piece reproducibility of the potentials of conventional electrodes.

Conclusions

The solid-contact electrode described in this paper can be used for reliable measurements of pH in acidic samples, including solutions containing HF. Unlike most of contemporary solid-contact ISEs with conducting polymers in the transducer layer, this electrode is stabilized with electron–ion-exchanger resin EI-21. This resin was not in use for the development of solid-contact electrodes for more than a decade being replaced with conducting polymers. However, use of this resin makes it possible to achieve rather good long-term stability and piece-to-piece reproducibility of the potentials.

Chronopotentiometric measurements showed that polarization at the interface between the membrane layer and the transducer layer is limited by diffusion. This polarization correlates with the long-term stability of the electrode potentials. In principle, this may be used as a criterion for prediction of the behavior of solid-contact electrodes with particular formulations of the transducer layers. However, the whole range of the polarization slopes except of that of coated-wire electrode is relatively narrow, so the found criterion is not very sensitive. Therefore, this finding, although promising, must be used very carefully.

References

1. Beliustin AA, Pisarevsky AM, Lepnev GP, Sergeev AS, Shultz MM (1992) Sens Actuators B 10:61
2. Schulthess P, Shijo Y, Pham HV, Pretsch E, Ammann D, Simon W (1981) Analyt Chim Acta 131:111
3. Erne D, Schenker KV, Ammann D, Pretsch E, Simon W (1981) Chimia 35:178
4. Oesch U, Brzozka Z, Xu A, Rusterholz B, Suter G, Pham HV, Welti DH, Ammann D, Pretsch E, Simon W (1986) Anal Chem 58:2285
5. Vishnevskij ME, Kapustin AM, Golubtsov AI, Sorokina GM (1987) Sov Electrochem 23:1232
6. Evsevleeva LG, Urusov YuI, Petrukhin OM (1993) Sov Electrochem 29:979
7. Burunkova YuE, Lutov VM, Mikhelson KN, Mukhacheva OV, Semenij VYa, Stefanova OK (1993) Ion Exchange and Ionometry 8:111
8. Egorov VV, Lutshik YaF, Novash VA (1996) Ion Exchange and Ionometry 9:59
9. Mi Y, Bakker E (1997) J Electrochem Soc 144:L27
10. Egorov VV, Sin'kevich YuV (1999) Talanta 48:23
11. Cho DH, Chung KC, Jeong SS, Park MY (2000) Talanta 51:761
12. Han WS, Park MY, Chung KC, Cho DH, Hong TK (2001) Electroanalysis 13:955
13. Dinten O, Spichiger UE, Chaniotakis N, Gehrig P, Rusterholz B, Morf WE, Simon W (1991) Anal Chem 63:596
14. Lutov VM, Mikhelson KN (1994) Sens Actuators B 18:400
15. Stefanova OK, Rozhdestvenskaya NV, Gorshkova VF (1983) Sov Electrochem 19:1225
16. Leis LHI, Saenko DV, Alagova ZS, Stefanova OK, Materova EA (1985) Cour St Petersburg Univ 25:9 (in Russian)
17. Stefanova OK, Rozhdestvenskaya NV, Muhitdinova BA, Bakirova RA, Ergozhin EE (1989) Russ J Appl Chem 62:995
18. Rozhdestvenskaya NV, Pugacheva EV (1992) Russ J Appl Chem 65:2205
19. Ivaska A (1991) Electroanalysis 3:247
20. Cadogan A, Gao Z, Lewenstam A, Ivaska A (1992) Anal Chem 64:2496
21. Bobacka J (1999) Anal Chem 71:4932
22. Markuzina NN, Mikhelson KN, Molodkina EV, Lewenstam A (2001) Russ J Appl Chem 74:409
23. Grekovich AL, Markuzina NN, Mikhelson KN, Bochenska M, Lewenstam A (2002) Electroanalysis 14:551
24. Michalska A, Appaih-Kusi C, Heng LY, Walkiewicz S, Hall EAH (2004) Anal Chem 76:2031
25. Lindfors T, Ivaska A (2004) Anal Chem 76:4387
26. Vazquez M, Bobacka J, Ivaska A (2005) J Solid State Electrochem 9:865
27. Sundfors F, Bereczki R, Bobacka J, Toth K, Ivaska A, Gyurcsanyi RE (2006) Electroanalysis 18:1372
28. Lindfors T, Aarnio H, Ivaska A (2007) Anal Chem 79:8571
29. Sjoeberg-Eerola P, Bobacka J, Lewenstam A, Ivaska A (2007) Sens Actuators B 127:545
30. Bobacka J, Ivaska A, Lewenstam A (2008) Chem Rev 108:329
31. Khripoun GA, Volkova EA, Liseenkov AV, Mikhelson KN (2006) Electroanalysis 13:1322
32. Lide DR (ed) (2002–2003) In: CRC handbook of chemistry and physics. CRC, Boca Raton, pp 8–44, 5–100
33. Bakker E (1996) J Electrochem Soc 143:L83
34. Bakker E (1997) Anal Chem 69:1061