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New Solid-State Contact for Ion-Selective Liquid Membrane Electrodes**

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Abstract. A new kind of solid-state contact for ion-selective electrodes based on solvent polymeric membranes is described. These electrodes show similar electrochemical behaviour to conventional ion-selective membranes in contact with an internal filling solution. They exhibit no significant interference with oxygen, nitrogen or carbon dioxide.

Introduction

First attempts of making electrochemical cells with incorporation of an intimate and thermodynamically well-defined contact between an electronic and a selective ionic conductor apparently reach back into the past century. There were studies of the behaviour of sodium-silicate glass layers that are on one side contacted with sodium amalgame and on the other side exposed to an aqueous solution. The aim was to demonstrate the ion-exchange properties of glass [1]. These ancient investigations have been the stimulating starting point for the later discovery of the pH-sensitive glass electrode. In the meantime, many different designs for such direct contacts between electronic conductors and ion-selective membrane materials were proposed [2]. Many of these approaches suffer from a thermodynamically ill-defined, unstable, or irreproducible potential difference at this interface, however. At least partly successful solutions to this problem include systems with solid-state membranes [3] [4], glass membranes [5] [6], and plasticized poly(vinyl chloride) membranes [7] [8].

Here, we report on novel ion-selective devices that combine neutral-carrier-based solvent polymeric membranes with internal solid-state contacting elements. The performance characteristics of these nearly all-solid-state sensors are comparable to the ones reported for conventional ion-selective electrodes with internal contact through electrolyte solutions.

Experimental

Preparation of the Electrodes. All electrodes were based on a Ag plate (purity 99.99%) with a diameter of 7 mm and a thickness of 0.5 mm. For the electrical contact, a 0.5-mm-diameter Ag wire is welded onto the backside of the plate. Before further preparation, the side of the plate contacting the membrane is roughened by using fine emery paper. All org. impurities were removed afterwards with conc. (56%) HNO_3 (*Suprapure®*, *Merck AG*, Darmstadt, FRG), and the plate was washed with doubly quartz-distilled H_2O and dried.

A AgI layer is built up by using electrolytic methods. For this purpose, the plates were dipped into a 1.87 wt-% HI soln. (*Suprapure®*, *Merck AG*, D-Darmstadt) and electrolysed during 2 h with a current of 1 µA/cm^2. The current was controlled with a constant power supply (type *NGPV 300/0.3*, *Rohde & Schwarz*, D-München and a *DMM* type *196* (*Keithley Instruments*, Cleveland, Ohio, USA). After electrolysis, the plates were cleaned twice with doubly quartz-distilled H_2O, then with EtOH (*puriss. p.a.*, *Fluka AG*, CH-9470 Buchs) and finally with CH_2Cl_2 (*puriss. p.a.*, *Fluka AG*, CH-9470 Buchs). Afterwards, they were dried in air at 20°.

On the AgI a graphite layer was formed with a colloidal suspension of graphite in H_2O (*Acheson Aquadag*, *Dr. Bender & Dr. Hobein AG*, CH-8042 Zürich) by using a paint brush. The graphite coating was then dried with a hair drier. Once the layer was dry, the plates were heated during 2 h at 150°. These graphite layers showed a thickness between 1.2 µm and 5.9 µm. They were doped with I_2 by exposing the graphitized plates to a sat. I_2 vapor atmosphere during 15 min at r.t.

Finally they were coated with 20 µl of a membrane cocktail prepared from 50.85 mg of the plasticizer BBPA (= bis(1-butylpentyl)adipate, *Fluka AG*, CH-9470 Buchs), 25.70 mg of poly(vinylchloride) (PVC hochmolekular, *Fluka AG*, CH-9470 Buchs) and 0.78 mg of the Na^+ selective ionophore *ETH 2120* [9] dissolved in 400 µl freshly distilled THF (*puriss. p.a.*, *Fluka AG*, CH-9470 Buchs). After evaporation of the solvent, the electrodes were stored during 2 d in air at r.t. under dust-free conditions.

EMF Measurements. The EMF measurements were performed at 20 ± 2° with FET operational amplifiers *AD 515 KH* (Analog Devices, Norwood, MA, USA, input impedance 10^{13} Ω/1.6 pF differential, 10^{15} Ω/0.8 pF common mode; input bias current < 75 fA; capacity neutralisation) as described in [10]. The measured EMF data were corrected for changes in the liquid-junction potential by using the *Henderson* formalism [11]. For the EMF measurements, the electrodes were incorporated into a flow-through-system especially designed for this purpose (see the *Fig.*). With a reference electrode described in [12] cells of the following type were finally used: Ag; AgI | graphite (I_2-doped) ‖ membrane ‖ sample solution | 1M LiOAc | KCl(sat.), Hg_2Cl_2; Hg.

Before the first measurement, all electrodes were conditioned with 0.1M NaCl soln. during at least three days, if not statet differently. All electrolyte solns. for conditioning and for the potentiometric measurements were prepared with doubly quartz-distilled H_2O and salts of *p.a.* grade (*E. Merck AG*, D-Darmstadt).

Results and Discussion

Stimulated by surprising results obtained during impedance measurements on ion-selective sensors, we systematically

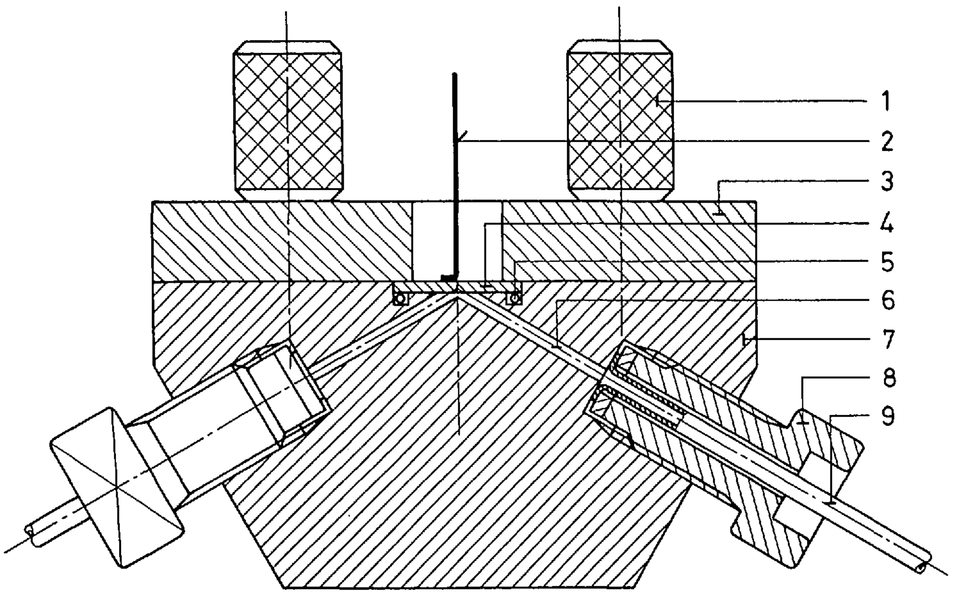

Figure. *Flow-Through Ion-Selective Electrode. 1* Screw for fixing the methacrylate cover 3 on methacrylate body 7. *2* Lead for electrically contacting the membrane support. *3* Cover plate (methacrylate). *4* Silver plate supporting the ion-selective membrane. *5* O-ring. *6* Flow-through channel. *7* Methacrylate body. *8* Fitting for sample inlet. *9* Sample inlet tube.

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Table 1. *Electrochemical Data of Different Types of Solid-State-Contacted Liquid Membrane Electrodes*

Type of contact[a])	Membrane [b])	Slope [c]) [mV]	Drift [d]) [mV/h]	Hysteresis with respect to Selectivity [mV]	Hysteresis with respect to Concentration [mV]	EMF Change in saturated solutions of O_2 [mV]	N_2 [mV]	CO_2[e]) [mV]
Ag/AgI		29.57 ± 5.09	–13.03	132.77	2.25	9.07	5.82	5.73
Ag/AgI	with I_2	54.34 ± 0.23	–1.27	26.28	18.52	1.67	2.46	4.63
Ag + G		53.88 ± 1.72	0.01	1.01	8.90	0.47	0.05	0.04
Ag + G	with I_2	53.15 ± 0.38	–0.28	1.17	17.48	3.42	2.28	1.21
Ag + GI		52.37 ± 1.06	0.15	5.31	9.13	1.92	0.42	2.77
Ag + GI	with I_2	51.32 ± 0.83	0.01	2.20	10.53	0.10	9.50	0.24
Ag/AgI + G		56.68 ± 0.11	–0.52	1.37	4.33	2.85	2.23	1.60
Ag/AgI + G	with I_2	55.54 ± 0.09	–0.36	10.64	13.26	0.49	6.69	12.13
Ag/AgI + GI		56.55 ± 0.12	–0.08	0.06	1.53	0.15	0.70	0.42
Ag/AgI + GI	with I_2	55.26 ± 0.35	–0.29	3.14	9.54	3.04	0.38	2.70
MEM No.*1*		57.22 ± 0.05	0.10	0.60	1.01			
MEM No.*2*		57.58 ± 0.53	0.10	2.20	2.30			
MEM No.*3*		57.78 ± 0.36	0.20	0.50	1.50			

[a]) G: with undoped graphite layer, GI: with I_2-doped graphite layer, MEM: conventional membrane arrangement with liquid internal filling solution.

[b]) Membrane composition: 66 wt-% of plasticizer (BBPA), 33 wt-% of PVC, 1 wt-% of *ETH 2120*. The membrane is selective for Na^+ ions. Membranes marked with I_2 contain 2×10^{-4} g I_2 per g membrane material.

[c]) Activity range for linear regression: – 4.0 to – 1.0 for log a_{Na}.

[d]) Drifts were determined after a conditioning time of at least 12 h in 0.1M NaCl.

[e]) Gas sensitivity tests were made by bubbling gas through the solution (0.1M NaCl) until saturated (normally during 30 min). No gas was bubbled through the solution during EMF measurement.

Table 2. *Electrochemical Behaviour of I_2-Doped and Undoped Solid-State Contacted and Conventional Membrane Electrodes*

log K^{pot}_{NaM}[a])	Undoped	Doped, after 1 day[b])	2 weeks[c])	4 weeks[d])	Liquid contact [15][e])
H^+	+ 1.81	– 1.25	– 0.92	– 0.38	– 0.7
Li^+	+ 1.64	– 1.32	– 1.20	– 1.20	– 1.2
K^+	+ 1.48	– 1.78	– 1.59	– 1.58	– 1.5
Ca^{2+}	+ 0.06	– 3.25	– 3.48	– 3.32	– 1.9
Mg^{2+}	– 0.85	– 4.20	– 3.53	– 3.12	– 3.9
Slope[f]) [mV]	55.0 ± 2.2	62.8 ± 0.1	56.6 ± 0.4	55.8 ± 1.1	57.4 ± 2.6

[a]) Standard deviation < 0.1, separate solution method on 0.1M chloride solutions.

[b]) Measured after one day of conditioning with 0.1M NaCl solution.

[c]) After two weeks in contact with different aqueous electrolytes as well as with proteins.

[d]) After further two weeks in contact with different aqueous electrolyte solutions.

[e]) Conventional solvent polymeric membrane contacted with liquid internal filling solution.

[f]) Theoretical slopes (20°): 58.2 mV, activity range for linear regression 10^{-4} to 10^{-1}M.

characterized several solid-state contacts for ion-selective solvent polymeric membranes containing neutral carriers. All of them were based on a Ag electrode as an electronic conductor and an intermediate graphite layer which could be doped with I_2. As an example of a neutral carrier, we choose the sodium-selective ionophore *ETH 2120* (*N,N,N',N'*-tetracyclohexyl-1,2-phenylenedioxydiacetamide [9] for all membranes. Experiments with ionophores selective for other ions are in progress. The electrodes were studied in view of: *a)* slope of the electrode response; *b)* long-time-drift; *c)* hysteresis in respect to concentration (*i.e.* difference in the EMF before and after measuring a range of concentrations of electrolyte solutions (here corresponding to changes from 10^{-1} to 10^{-4} M NaCl and comparison of measurements in the 10^{-1} M solution)); *d)* hysteresis in respect to selectivity (*i.e.* difference in the EMF of two measurements in the 10^{-1} M NaCl solution before and after measuring different electrolyte solutions (here KCl, LiCl, HCl, $CaCl_2$, $MgCl_2$) at a given concentration (here 10^{-1} M)); *e)* selectivity; *f)* influence of different gases on the electrode potential (in view of the well-known influences of reductive and oxidative gases reported in [13] (see also [14])). All the data were compared with those obtained on conventional ISE's with the same membranes which, however, were contacted with an aqueous internal filling solution (the membranes were incorporated in *Phillips IS 560* electrode bodies according to [12]).

Table 1 shows electrochemical data of different types of solid-state sensors tested. Best results in respect to low drift of the potential, small hysteresis, and nearly no influence of O_2, N_2, and CO_2 were obtained with the combination of a Ag, AgI half cell and a I_2-doped graphite layer.

As shown in *Table 2*, the doping of graphite with I_2 seems to have a big influence on the selectivity. The selectivity obtained for the doped graphite layer is comparable with conventional electrodes and in the case of doubly charged ions it is even far superior. The electrode with the undoped graphite layer shows almost no selectivity.

The only disadvantage so far found for these new devices is the rather long conditioning time of the membranes which may exhibit super-nernstian slopes even after a conditioning during more than three days.

A tentative explanation of the high potential stability achieved for the present contacting system suggests the formation of polynuclear, lipophilic anions of the type I_3^- or I_5^- in equilibrium with the native components I_2 and I^-. Correspondingly, a thermodynamically well-defined interfacial potential contribution between organic membrane phase and solid reference electrode could be established.

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