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Application of a New pH-Sensitive Electrode as a Detector in Flow Injection Potentiometry

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Abstract
A new pH sensitive detector for flow-through potentiometry was developed on the basis of a graphite/quinhydrone composite electrode. The detector was constructed of two polymethylmethacrylate plates between which a 0.1 mm thick sensitive layer is situated. After drilling a hole through the plates, a ring of the sensitive layer is exposed to the solution stream. A conventional calomel reference electrode was placed downstream following the flow-through sensor. The response behavior in different electrolyte solutions was investigated. The detector shows a Nernstian behavior for injections of hydrochloric acid into a KCl background solution as well as for the steady state response in concentration step experiments using hydrochloric acid and buffer solutions. The response time is sufficiently short for FIA applications (T_{95} between 3 and 5.4 s). The influences of flow rate and injection volume on the detector signal are discussed.

Keywords: Potentiometric flow cell, pH measurements, Flow injection analysis

1. Introduction

The determination of pH of solutions is one of the most frequent tasks in analytical laboratories. For this a large arsenal of methods is available, as, e. g., pH papers, indicator solutions, optrodes, and potentiometric sensors as glass electrodes, metal-metal oxide electrodes, pH-dependent redox electrodes like the quinhydrone electrode etc.

Because of the large number of pH measurements, very early a strong demand was felt for automatization. Flow injection analysis (FIA) has an outstanding position in the field of automation of analyses. Several detection techniques have been utilized in FIA: photometry, fluorimetry, atomic absorption spectroscopy, refractometry, ICP and electrochemical techniques like amperometry, voltammetry and potentiometry [1]. As Cammann has pointed out [2], potentiometry with ion-selective electrodes offers several advantages, among them the small dead volume, the simple and inexpensive instrumentation and the wide accessible concentration range. In flow-through potentiometry it is demanded that the indicator electrode gives a fast response in a reproducible form. In batch measurements as well as in flow injection potentiometry used for pH measurements different pH sensitive indicator electrodes have been described in the literature such as glass electrodes [3], PVC or epoxyacrylate membranes [4, 5], ion selective electrodes in combination with dialysis tubes [6], metal/metal oxide electrodes [7, 8], pH sensitive ISFETs [9] and stainless steel electrodes [10]. Glass electrodes are comparably expensive and are difficult to arrange in flow-through

systems. PVC membranes and other ion-selective electrodes very often possess long response times which is a drawback in flow-through systems. The chemical stability of metal-metal oxide electrodes as well as the stainless steel electrode is not sufficient, especially in acidic solutions. As an alternative in batch experiments, it has been shown in earlier studies [11, 12], that composite electrodes based on quinhydrone are useful for calibration free measurements in solutions with pH values up to 8.5. These electrodes have the same properties as a conventional quinhydrone electrode, i.e., Nernstian behavior, short response time etc., but additionally they can be used in emulsions, and they can be produced as very robust electrodes.

The aim of the present work was the application of that sensor material to construct a new potentiometric detector for FIA systems. The new detector cell was characterized with respect to response time, response behavior in different electrolyte solutions at different flow rates, long term stability etc.

2. Experimental

2.1. Cell Construction

Figure 1 shows schematically the construction of the detector cell. It consists of a polymethacrylmethacrylate plate (A). A Copper spacer frame (B) is placed on that plate, the thickness of which defines the thickness of the sensing layer (in present studies: 0.1 mm). The rectangular copper frame
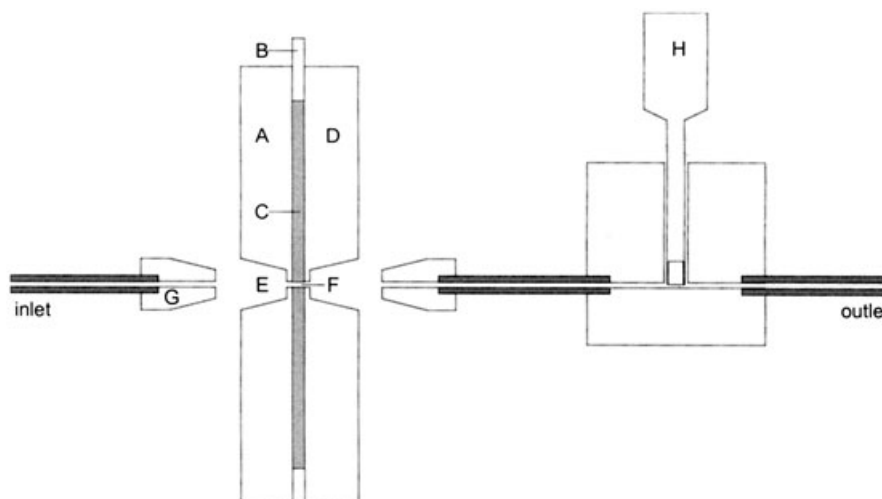
Fig. 1. The detector cell: A) and D) polymethylmethacrylate plates, B) copper spacer frame, C) pH sensitive layer, E) hole for the FIA fittings, F) hole through the pH sensitive material, G) FIA tubes with fittings, H) reference electrode.

was made from a copper plate with the given thickness and a size of 120×30 mm and frame width of 7 mm. Contacting this frame to the electrode channel of the measurement equipment gives the electric contact to the sensitive layer during the experiment. The copper frame is not in contact with the solution. The sensitive layer (C) was prepared by milling quinhydrone and surface oxidized graphite powder in a ratio 1:1 in a ball mill. The surface oxidation of the graphite powder is necessary to ensure the reversibility of the quinhydrone as the pH-sensing material [11, 12]. To one part of quinhydrone/graphite mixture one part prepolymerized polymethylmethacrylate was given in a mortar and approximately 2 parts of liquid methylmethacrylate were added to form a paste. This paste was evenly distributed on the polymethacrylmethacrylate plate. A second polymethacrylmethacrylate plate (D) was pressed onto that layer in such a way that no air bubbles were included in the pH sensitive layer. The sensitive layer was allowed to polymerize and harden for two days. Before measurements, conic holes (E) were drilled into the polymethylmethacrylate plates from both sides to connect the cell with FIA tube fittings (G). A cylindrical hole was drilled with a 0.5 mm driller through the sensing material (F). The reference electrode (H) was arranged as close as possible downstream of the pH-sensing layer.

2.2. Equipment

A 708 Sampling Unit (Metrohm, Herisau, Switzerland) provided the pump and 6-port valve. Two flow rates could be realized by changing the tubing of the pump: 1.22 mL $\cdot$ min^{-1} and 3.94 mL $\cdot$ min^{-1}. The flow through cell and the reference electrode were arranged shortly after the valve. The reference electrode was a KE 10 saturated calomel electrode ($E = 244.4$ mV at 25 °C) (Sensortechnik Meinsberg, Meinsberg, Germany).

Potentiometric measurements were recorded using an AUTOLAB with a PGSTAT 20 (Eco-Chemie, Utrecht, The Netherlands) in conjunction with a personal computer (IBM compatible).

The pH values of the solutions were measured with an EGA 151 combination glass electrode (Sensortechnik Meinsberg, Meinsberg, Germany) connected to a WTW 3440 i pH-meter (WTW, Weilheim, Germany).

2.3. Chemicals

A 1 mol $\cdot$ L^{-1} hydrochloric acid solution was prepared as stock solution from an ampule and diluted when necessary. As buffer solutions Merck CertiPur solutions pH 2, 4, 6, 7 and 8 were used. KCl, conc. HNO$_3$ and quinhydrone were of p.a. quality. Graphite powder was of "purissimum" quality. All these chemicals were purchased from Merck, Germany.

As binder for the sensitive layer Orthocryl CE from Dentaurum, Germany, a two component polymethylmethacrylate resin, was used.

3. Results and Discussion

3.1. Response Behavior in Different Electrolyte Solutions

To determine the conductivity of the background electrolyte which is necessary to obtain a good signal-to-noise ratio, KCl solutions of different concentrations were employed. As mentioned in [4] an ionic strength of 0.01 M to 0.1 M should be maintained to get a well defined baseline. In addition, the buffer capacity of the carrier solution β_c should be as small as possible compared to the buffer capacity of the sample β_s [13]. An unbuffered KCl solution has a very low buffer capacity. 0.05 M or 0.1 M KCl solutions as carrier solutions have an ionic strength frequently used in other
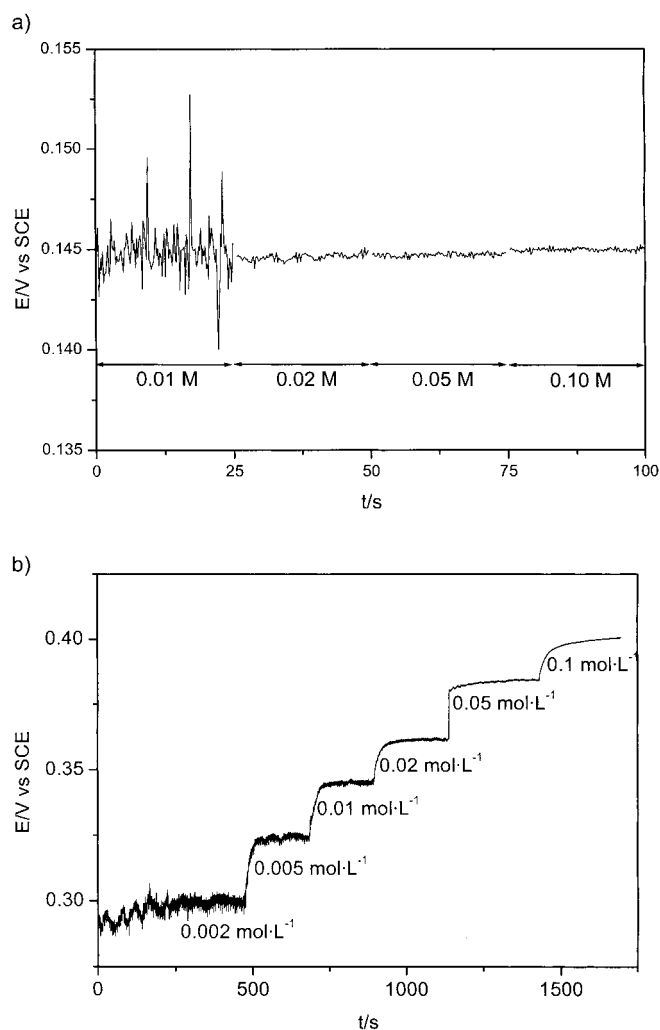
a)

b)

Fig. 2.   a) Cell response in KCl solutions of different concentrations (flow rate $1.22\ \mathrm{mL \cdot min^{-1}}$). b) Cell response in hydrochloric acid solutions of different concentrations (flow rate $1.22\ \mathrm{mL \cdot min^{-1}}$).

Fig. 3.   pH dependence of cell potential in hydrochloric acid and KCl solutions.

FIA set-ups [4, 13, 14]. Figure 2a shows that a well defined baseline is obtained only at concentrations higher than $0.01\ \mathrm{mol \cdot L^{-1}}$ (flow rate: $1.22\ \mathrm{mL \cdot min^{-1}}$). Using KCl solutions in a concentration range from 0.01 M to 0.1 M as carrier solutions the baseline noise can be reduced from $\pm 6\ \mathrm{mV}$ at 0.01 M KCl to $\pm 0.2\ \mathrm{mV}$ at 0.05 M and 0.1 M KCl. The baseline noise at higher KCl concentrations is comparable to other FIA setups with wall-jet detectors [14] (noise: $\pm 0.3\ \mathrm{mV}$) or pH-ISFETs [4] (noise: less than $\pm 0.2\ \mathrm{mV}$).

A Fourier analysis of the noise showed a distinct contribution at 2.0 Hz which may be caused by the electric circuit. Additionally, a contribution at 0.15 Hz is attributed to the pump, respectively.

A similar behavior was observed in hydrochloric acid solutions of different concentrations (flow rate: $1.22\ \mathrm{mL \cdot min^{-1}}$) (cf. Fig. 2b). In that case, rather smooth baselines were obtained at concentrations higher than $0.002\ \mathrm{mol \cdot L^{-1}}$. The potentials obtained in the flow-through system with

different hydrochloric acid and 0.1 M KCl solutions (pH 5.41) were plotted versus the pH values determined in batch experiments with a conventional glass electrode (cf. Fig. 3). A linear function was obtained with a slope of $-57.6\ \mathrm{mV \cdot (pH)^{-1}}$ and a potential of $E_{\mathrm{pH=0}} = 459.1\ \mathrm{mV}$ when the curve is extrapolated to pH = 0. This is in satisfactory agreement with the theory of the conventional quinhydrone electrode (slope $-59.2\ \mathrm{mV \cdot (pH)^{-1}}$, $E_{\mathrm{pH=0}} = 455.4\ \mathrm{mV}$). Figure 4 depicts the response when different buffer solutions pass the detector. The inset in Figure 4 gives the dependence of the obtained potential on the pH of the buffer solutions. In that case a linear dependence was obtained with a slope of $-57.9\ \mathrm{mV \cdot (pH)^{-1}}$ and $E_{\mathrm{pH=0}} = 450.0\ \mathrm{mV}$. The results were practically independent of the flow rate, i.e., there were only small differences of the obtained potential (about 1 mV at pH 4 and 6) between both flow rates ($1.22\ \mathrm{mL \cdot min^{-1}}$ and $3.94\ \mathrm{mL \cdot min^{-1}}$). Figure 5 shows the successive injection of 50 μL of hydrochloric acid of different concentrations into a background solution of $0.1\ \mathrm{mol \cdot L^{-1}}$ KCl. The peak shape is controlled by convection and diffusion [15, 16]. The same experiment was done with an injection volume of 850 μL to obtain steady state conditions. By plotting the potential versus the pH of the injected solution it can be seen that the potential increases linearly with increasing concentration of hydrochloric acid with a slope of $-50.6\ \mathrm{mV/pH}$ (injection volume 50 μL) and $-53.7\ \mathrm{mV/pH}$ (injection volume 850 μL). Extrapolation leads to $E_{\mathrm{pH=0}} = 417.0\ \mathrm{mV}$ (50 μL injection) and $E_{\mathrm{pH=0}} = 434.8\ \mathrm{mV}$ (850 μL injection). The obtained slopes are comparable to the slopes observed in other FIA experiments coupled with pH detection (sensitivity from 51.8 mV/pH to 56.9 mV/pH) [3, 6, 10, 13, 14].

3.2. Response Time

The response time was determined by a sudden change of the background solution from $0.1\ \mathrm{mol \cdot L^{-1}}$ KCl to a buffer solution with pH 2 and pH 8, respectively, at different flow
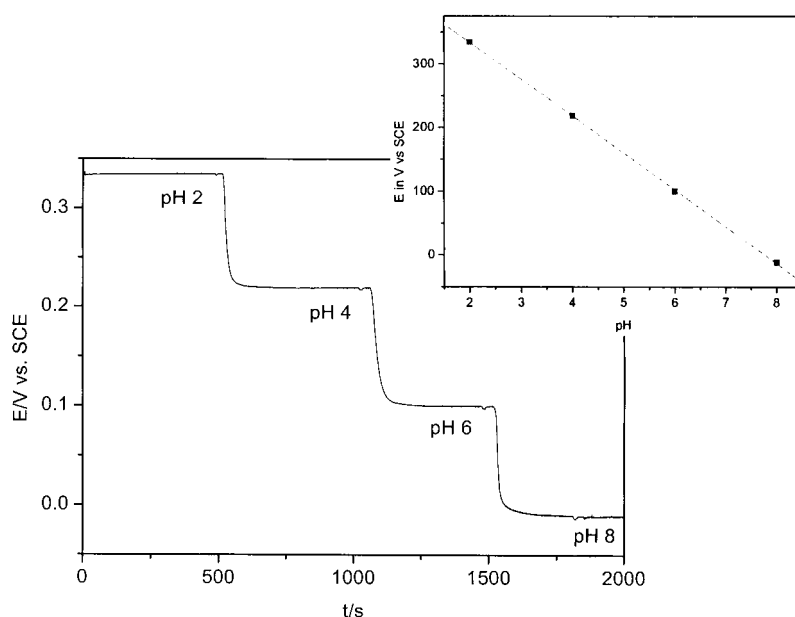
Fig. 4. Cell response in different buffer solutions (flow rate 3.94 mL · min⁻¹). Inset: pH dependence of cell potential.

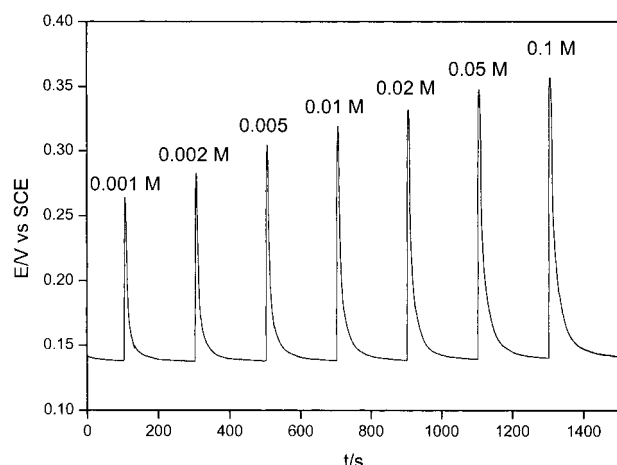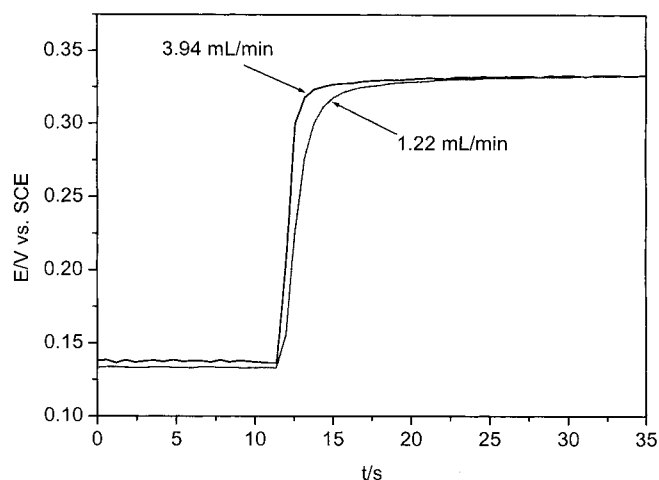Fig. 5. Successive injection of different HCl concentrations. Injection volume: 50 μL, carrier solution: 0.1 mol · L⁻¹ KCl, flow rate: 1.22 mL · min⁻¹.

Fig. 6. Response behavior of the detector cell for changing the electrolyte solution from 0.1 mol · L⁻¹ KCl to a buffer with pH 2.

Table 1. Time constants τ, delay time T_m and T_{95} of cell response behavior for flow rates 1.22 mL · min⁻¹ and 3.94 mL · min⁻¹.

Flow rate (mL · min⁻¹)	1.22	3.94
T_m in (s)	0.5	0.0
τ (s)	1.3	0.9
T_{95} (s)	5.4	3.0
v_r (mL)	0.02	0.06

rates (cf. Fig. 6). The response curves could be described by a first-order differential equation and assuming a delay time. The time constants were evaluated according to [16]:

$$E = E_a + \Delta E \ (1 - \exp\{-(t - T_m)/\tau\}) \tag{1}$$

where E is the potential at time t, E_a is the start potential, ΔE the potential difference between the maximum potential and E_a, τ is the time constant, and T_m is the delay time. They are listed in Table 1 together with the T_{95} times, and the response volumes v_r. The latter were calculated as $v_r = \tau \cdot f$ (*f*-flow rate) [18].

3.3. Influence of Flow Rate and Injection Volume

To determine the influence of the injection volume on the peak shape, different volumes of a 0.1 mol · L⁻¹ HCl were injected into a background solution of 0.1 mol · L⁻¹ KCl. The flow rate was 1.22 mL · min⁻¹. The obtained signals are depicted in Figure 7. For injection volumes between 50 μL to 250 μL a nonsteady state response was observed controlled by convection and diffusion. At higher injection volumes, steady state conditions were reached. The same experiment was repeated with the higher flow rate of 3.94 mL · min⁻¹. Here, the obtained peaks are sharper compared to those obtained at the lower flow rate, i.e., the
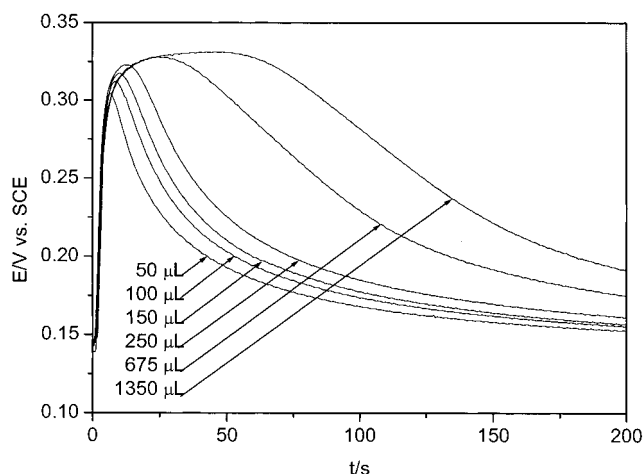
Fig. 7. Influence of the injection volume on the peak shape (flow rate: 1.22 mL·min^{-1}).

slope is steeper and the peak-width is smaller. The peak heights are less in case of the higher flow rate.

3.4. Long-Term Stability

Long-term stability was investigated by injecting 50 μL of a 0.1 mol·L^{-1} hydrochloric acid in 125 s intervals into a 0.1 mol·L^{-1} KCl background solution (Fig. 8). The peak height constantly decreases with the number of injections (about -0.125 mV/injection at 1.22 mL·min^{-1} and -0.335 mV/injection at a flow rate of 3.94 mL·min^{-1}). The baseline drift of 0.8 mV/h is in an acceptable range compared to other FIA set-ups [4], which show a drift of about 1 mV/h. The long-term stability is satisfactory provided that two point calibrations are used for analyses.
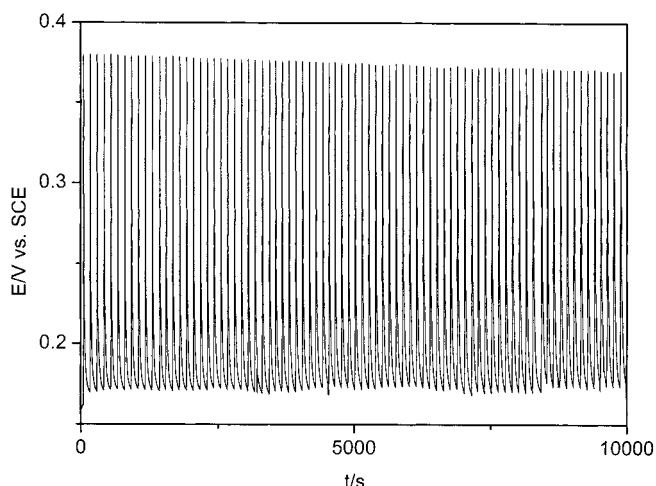
Fig. 8. Dependence of the cell response on the measuring time. Injection volume: 50 μL 0.1 mol·L^{-1} hydrochloric acid, interval: 125 s, carrier solution: 0.1 M mol·L^{-1} KCl, flow rate: 1.22 mL·min^{-1}.

3.5. Injection Frequency

Examination of the peak shape obtained from the first peaks of the longtime experiments gave a time interval of 125 s at a flow rate of 1.22 mL·min^{-1} or 60 s at a flow rate of 3.94 mL·min^{-1} between injecting the sample and return of the potential to the baseline. From these time intervals injection frequencies of 29 injections/h and 60 injections/h at flow rates of 1.22 mL·min^{-1} and 3.94 mL·min^{-1}, respectively, were calculated for 50 μL injections of 0.1 mol·L^{-1} hydrochloric acid into a 0.1 mol·L^{-1} KCl solution.

4. Conclusions

In the present work, a new pH detector for FIA experiments has been developed on the basis of graphite/quinhydrone composite material. With this sensor, the pH of samples can be recorded in a simple, quick and reproducible way. Because the sensor material is well known to be applicable in real samples like emulsions, it opens a wide range of applications. By using the FIA technique, an automatization of pH measurement as well as the recording of processes accompanied with a pH change are possible. Studies to use this detector for FIA titrations are in progress.

5. Acknowledgements

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