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ARTICLE *in* ANALYTICAL CHEMISTRY · SEPTEMBER 2004

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# Stability of the Inner Polyaniline Solid Contact Layer in All-Solid-State $K^+$ -Selective Electrodes Based on Plasticized Poly(vinyl chloride)

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**A simple and powerful method based on UV–visible spectroscopy is presented for studying the stability of the inner electrically conducting polyaniline (PANI) solid contact (SC) layer in all-solid-state ion-selective electrodes (ISE). The influence of the plasticized poly(vinyl chloride) (PVC) membrane (ISM) composition and the pH of the sample solution on the stability of the solid contact is reported. PANI is used as a model compound in this study, but the method presented is universal and can be applied to different types and combinations of SCs and ISMs. It provides a tool for finding the best combination of conducting polymer and ISM for solid contact ISEs. PANI is deposited electrochemically either on glassy carbon or quartz glass covered with a thin layer of tin oxide, and a  $K^+$ -selective ISM is deposited on top of the PANI layer. The short-term stability of the inner PANI layer is good for all membrane types in buffer solutions with pH 2, 6, and 9, indicating that the outer plasticized PVC membrane hinders the emeraldine salt–emeraldine base transition of the highly pH sensitive PANI layer. The solid contact  $K^+$ -selective electrodes studied showed a Nernstian response of  $58.2 \pm 0.1$  mV/log  $a_K$ . Significant differences are observed in the long-term stability of the inner PANI layer between the different membrane types. This indicates that water uptake of the PVC membrane and its permeability to  $OH^-$  ions are critical parameters affecting the stability of the PANI layer. The solid contact electrodes based on PANI may require a composition of the PVC membrane different from those typically used in conventional ISEs with an inner solution.**

The solid contact (SC) all-solid-state ion-selective electrode (ISE) concept with an electrically conducting polymer (CP) as the ion-to-electron transducer between the ion-selective membrane (ISM) and the metal substrate was introduced a decade ago and is now studied by many research groups working with ISEs.<sup>1</sup> The CP layer converts the ionic conduction to an electronic signal due to its reversible oxidation–reduction reaction and has the same function as the Ag|AgCl wire in conventional ISEs. The redox reaction of the CP is accompanied by insertion/expulsion of

anions/cations/electrons depending on the composition of the CP layer.

The CPs cannot directly be used as such as membrane materials in ISEs due to their nonselective properties<sup>1</sup> even though there are some exceptions.<sup>2–4</sup> They are therefore suitable as sublayer (solid contact) materials that are not in direct contact with the sample solution. It is very important that the CP solid contact is stable and chemically inert when the ISM is contacted with different sample solutions. The long-term stability of the ISE can be affected, for example, by water uptake of the ISM and its chemical stability. Changes in the sample solution composition are also reflected at the ISM|CP interface, which may undergo chemical changes and therefore affect the ISE response (potential). It has recently been reported that a thin aqueous layer is formed between the ISM and a Au substrate, causing a drift in the electrode potential, which can be avoided by depositing a lipophilic self-assembled monolayer on the Au surface.<sup>5</sup>

The most common solid contact materials are polypyrrole (PPy),<sup>1,6–19</sup> polyaniline (PANI),<sup>20–27</sup> poly(3,4-ethylenedioxythiophene)

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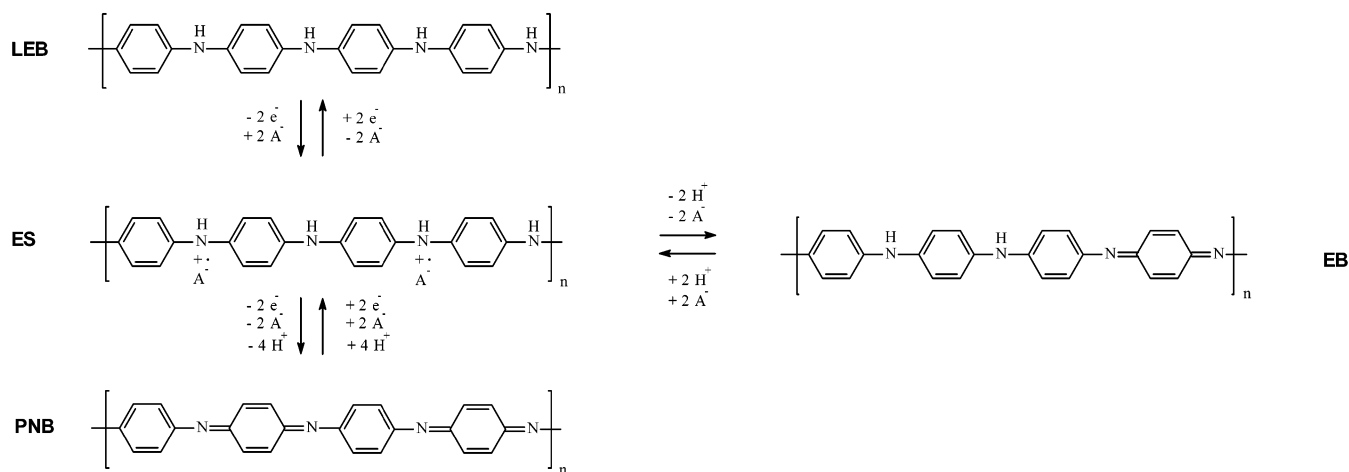


Figure 1. Redox mechanism among the LEB, ES, and PNB forms of PANI and the pH-dependent transition between the ES and EB forms.

(PEDOT),<sup>28–34</sup> and polythiophene derivatives, e.g., poly(3-octylthiophene) (POT).<sup>35–38</sup> They are usually electrochemically deposited on electrically conducting substrates (Au, Pt, or glassy carbon, GC) from aqueous solutions, although there are a few exceptions where organic solvents<sup>18,35,37</sup> or soluble CPs (PANI and POT)<sup>24,27,36,38</sup> have been used for the deposition of the inner solid contact layer. Water will always be present at the ISM|CP and CP|substrate interfaces after depositing the inner SC layer from aqueous solutions. The formation of a water layer at the ISM|CP interface can therefore be avoided during the preparation process of the solid contact by performing the electropolymerization in organic solvents or by using solid contact layers that are prepared from

CPs, e.g., PANI and POT, which can be solubilized in organic solvents. In the latter case, the solid contact layer is deposited by spin or drop casting on the substrate material. This might improve the long-term potential stability of the solid contact electrodes. The drawback of soluble CPs is, however, that they might be mixed with the ISM membrane when drop casted on top of the CP layer resulting in a poorly defined ISM|CP interface with low reproducibility. It should also be pointed out that the influence of the drying step of the CP layer on the long-term stability of the solid contact electrodes is not very well understood at the moment. A drying step is normally required before the ISM can be drop casted on top of the CP layer.

PANI is one of the most studied CPs due to its high stability, easy preparation procedure from acidic aqueous solutions, relatively low cost monomer, solubility in many organic solvents, and processability with commonly used bulk polymers such as polyethylene, polypropylene, poly(methyl methacrylate), and poly(vinyl chloride) (PVC).<sup>39</sup> It is therefore possible to prepare PANI films both from aqueous and from organic solvents. PANI is also known to be a very pH sensitive material (the only intrinsically ion-selective CP), in contrast to poly(*N*-alkylanilines),<sup>40</sup> due to the pH-dependent emeraldine salt (ES)–emeraldine base (EB) transition (Figure 1).<sup>4,20,41</sup> Depending on the type of PANI, the electrically conducting ES form is usually stable at pH ≤ 4 and the nonconducting EB form at pH ≥ 7–8. In the mid-pH range, a mixed ES–EB form is obtained. We have recently showed that the pH sensitivity of films prepared from soluble PANI can be suppressed or even eliminated by the addition of anionic lipophilic additives to the film.<sup>42</sup> In comparison to the electrochemically prepared PANI, the lipophilicity of films prepared of soluble PANI can be influenced with appropriate additives.

In the present paper, the influence of the solution pH on the stability of the PANI solid contact has been studied with UV–visible spectroscopy. The solution pH is varied between pH 2 and 9, and the PANI film is prepared electrochemically in an aqueous solution of 1.0 M HCl in order to prevent mixing of the CP and ISM phases. The method presented is universal, and its novelty

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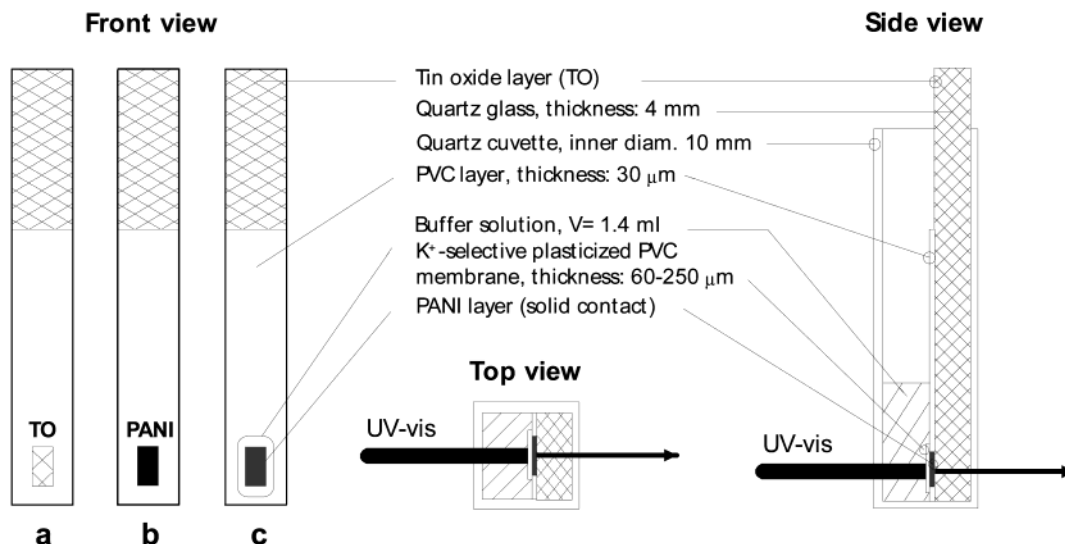


Figure 2. Front view of the quartz glass, which is covered with a thin layer of TO and PVC, during the different preparation steps of the K<sup>+</sup>-sensitive solid contact electrode: (a) before and (b) after deposition of the PANI(Cl) layer on TO and (c) the PANI(Cl) layer coated with a K<sup>+</sup>-sensitive plasticized PVC membrane (solid contact configuration). The top and side views of the experimental setup of the UV–visible measurements for the solid contact electrodes are also shown in the figure.

is based on the possibility of measuring the UV–visible absorbance spectrum of only the inner PANI layer in the solid contact configuration. The absorbance of plasticized PVC is negligible in the studied wavelength region (340–1100 nm) and can be background corrected in a double-beam spectrophotometer. For the first time, direct evidence of long-term chemical changes of the solid contact layer is reported.

## EXPERIMENTAL SECTION

**Chemicals.** Aniline, high molecular weight PVC (HMW PVC), bis(2-ethylhexyl) sebacate (DOS), valinomycin, and potassium tetrakis(4-chlorophenyl) borate (KTPCIPB) were obtained from Fluka. Special care should be taken when handling the highly toxic valinomycin. The buffer solutions used in both potentiometric and UV–visible measurements were prepared according to Perrin and Dempsey.<sup>43</sup> These solutions consisted of 25 mM citric acid (monohydrate) ( $\geq 99.5\%$ ), 25 mM Tris (p.a.  $\geq 99.8\%$ ), 25 mM KCl (p.a.  $\geq 99.5\%$ )—obtained from Fluka—25 mM KH<sub>2</sub>PO<sub>4</sub>, and 25 mM NaB<sub>4</sub>O<sub>7</sub>·10 H<sub>2</sub>O (Merck). The pH of the buffer solution was adjusted to the desired pH value either with HCl or with NaOH. Separate buffer solutions for each pH were prepared covering the pH range from 2 to 9. All aqueous solutions used in this study were prepared from distilled-deionized water with resistance of  $\geq 18.2$  MΩ.

**Polymerization of Aniline.** Aniline was polymerized in a 1.0 M HCl solution in the potential interval of  $-0.2$  to  $+0.82$  V (vs SCE) on two different electrode substrates: GC (0.05 M aniline, 100 cycles) and tin oxide (TO) (0.1 M aniline, 70 cycles);  $\nu = 50$  mVs<sup>-1</sup>. These films will hereafter be referred to as PANI(Cl).

The TO glasses, which were used in the UV–visible measurements, were modified in the following way before the polymerization of aniline. The surface of the electrically conducting TO glass was first covered three times with a thin layer (total thickness  $\sim 30$  μm) of PVC (13.1% (m/m) in cyclohexanone) using

a small brush. A small rectangular area of  $\sim 3$  mm  $\times$  6 mm (0.18 cm<sup>2</sup>), which was in the height of the light path of the UV–visible spectrophotometer, was left uncovered with PVC (Figure 2, front view, a). The TO glasses were cleaned with dishwashing detergent, washed with plenty of twice distilled-deionized water (resistance  $\geq 18.2$  MΩ), and dried before the PVC layer was applied on top of the TO glass surface. The PVC layer was allowed to dry overnight before a PANI(Cl) film was polymerized on the uncovered rectangular area of the TO glass (Figure 2, front view, b). The GC disk electrodes with poly(tetrafluoroethylene) bodies, which were used in the potentiometric measurements, had a surface area of  $A = 0.07$  cm<sup>2</sup>. They were polished with 0.3-μm Al<sub>2</sub>O<sub>3</sub> powder and rinsed with deionized water prior to the polymerization. All solutions were purged with N<sub>2</sub> for 20 min prior to use. During the polymerization and characterization, the solutions were blanketed with N<sub>2</sub>. The PANI(Cl) films were always conditioned overnight in 0.1 M HCl prior to any potentiometric and UV–visible measurements or before the K<sup>+</sup>-selective membrane was applied on the top of the PANI(Cl) film.

**Solid Contact Electrodes.** Three different types of PVC membranes with the following composition (m/m) were deposited on the top of the TO/PANI(Cl) and GC/PANI(Cl) layers: Membrane 1 (M1): 1.0% valinomycin (K<sup>+</sup>-selective ligand), 0.5% KTPCIPB, 65.5% DOS, and 33.0% HMW PVC. Membrane 2 (M2): 1.0% valinomycin, 66.0% DOS, and 33.0% HMW PVC. Membrane 3 (M3): 67.0% DOS and 33.0% HMW PVC (i.e., only plasticized PVC). The membrane components were dissolved in 6 mL of THF. The PANI(Cl) electrodes, which had been conditioned in 0.1 M HCl overnight, were dried in air for 1 h (not rinsed with deionized water in order to prevent the ES–EB transition) before the membranes M1–M3 were applied on top of the PANI(Cl) layer. The M1–M3 solution ( $2 \times 40$  μL) was drop casted on the top of the TO/PANI(Cl) electrodes to obtain membranes with a thickness of  $\sim 250$  μm. M1 membranes with a thickness of  $\sim 60$  μm (20 μL solution) were also prepared in order to study the influence of the film thickness on the stability of the inner PANI(Cl) layer.

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The M1–M3 solution ( $2 \times 30 \mu\text{L}$ ) was applied on the GC/PANI(Cl) electrodes resulting in a membrane thickness of  $\sim 400 \mu\text{m}$ . The film thickness of the inner GC/PANI(Cl) and TO/PANI(Cl) layers was not varied in this study.

THF was allowed to evaporate for 4 h from the M1–M3 membranes before they were conditioned in 0.1 M KCl overnight prior to potentiometric and UV–visible measurements.

**UV–Visible Measurements.** The UV–visible spectra of the TO/PANI(Cl) film were measured in separate buffer solutions with pH 2–9. The spectra were always recorded from pH 2 to 9 and taken after an equilibration time of 15 min. The experimental setup is the same as shown for the solid contact electrode in Figure 2 (top and side views). The background spectra were determined with two TO glasses coated with PVC but without a PANI(Cl) film (Figure 2, front view, a).

Two different types of UV–visible measurements were made with the solid contact TO/PANI(Cl) films that were covered with the M1–M3 membranes. Type 1: The short-term stability of the PANI solid contact electrodes was determined during 19 h in 1 mM KCl (pH  $\approx 5.5$ ) and in buffer solutions with pH 6, 2, and 9 in the given order. The electrode membranes had not been in contact with aqueous solution prior to the short-term stability tests. Type 2: The long-term stability of the different solid contact electrodes was measured in 1 mM KCl during 1–3 months. The background spectrum was always determined in the test solution with two TO glasses (without a PANI(Cl) film; Figure 2, front view a) that were coated with the M1 membrane ( $2 \times 40 \mu\text{L}$ ).

All UV–visible spectra were recorded with a Hitachi U-2001 spectrophotometer, and a syringe was used to manually fill the cell with  $1400 \mu\text{L}$  of the test solution and to remove the previous solution from the cell. All experiments were performed at  $23 \pm 1^\circ\text{C}$ .

**Potentiometric Measurements.** Potentiometric measurements were done only with the PANI(Cl) and solid contact electrodes prepared on GC. These electrodes were used as indicating electrodes and a SCE as the reference electrode. Three identical electrodes were always prepared, and the potential readings were taken after 5 min in quiescent solution (3 min stirring).

For the GC/PANI(Cl) electrodes, only the potentiometric pH sensitivity was measured in buffer solutions with pH 2–9. The electrodes were always calibrated from pH 2 to 9 and then back to pH 2. The mean value of the potential readings at the different pH values was used to calculate the slope of the calibration plot.

The  $\text{K}^+$  sensitivity of the solid contact electrodes was measured in  $10^{-1}$ – $10^{-6}$  M KCl solutions. The electrodes were always calibrated from low concentration to high and back to low. The mean value of the potential readings at the different  $\text{K}^+$  concentrations was used to calculate the slope of the calibration plot ( $10^{-1}$ – $10^{-4}$  M). All potential readings reported were corrected for the liquid junction potential with the Henderson equation, and the activity coefficients were calculated with the Davies equation.<sup>44</sup>

The potentiometric pH and  $\text{CO}_2$  sensitivity of the solid contact electrodes prepared with the M1 membrane was measured in a 1 mM KCl solution. The electrodes were calibrated in  $10^{-1}$ – $10^{-6}$

M KCl solutions (same procedure as above)—giving a  $\text{K}^+$  sensitivity of  $58.2 \pm 0.1 \text{ mV/log } a_{\text{K}^+}$ —prior to the pH sensitivity test, which was done in the pH interval of 2–10. The potentials of the solid contact electrodes were first measured in 1 mM KCl (pH  $\approx 5.5$ ) during 10 min (5 min stirring) before pH was adjusted with HCl to pH 2. The potential was then always measured for 20 min (10 min stirring) at the desired pH value before increasing it with NaOH. pH was continuously measured with a Metrohm glass pH electrode (model 6.0232.100) during the measurement. After the pH test, the solid contact electrodes were equilibrated in 1 mM KCl for 30 min prior to the  $\text{CO}_2$  test.  $\text{N}_2$  was continuously purged through the solution for 2 h during the  $\text{CO}_2$  test. The electrode potentials were measured during both equilibration in 1 mM KCl and the  $\text{CO}_2$  test.

The potential stability of the solid contact electrodes with the M1 membranes was measured in a 1 mM KCl test solution at  $25 \pm 0.1^\circ\text{C}$  for 1 month. The SCE was separated from the test solution with a bridge filled with 1 mM KCl, and the solid contact electrodes were always stored in a fresh 1 mM KCl solution between the stability measurements, which were done in fresh test solutions.

## RESULTS AND DISCUSSION

**PANI(Cl) Films.** The cyclic voltammograms (CVs) recorded during the polymerization and characterization of the PANI(Cl) films in 1.0 M HCl are shown in Figure 3. It is well known that PANI has a more complex electrochemistry than other CPs (Figure 1), and it is generally agreed that PANI has three oxidation states (the abbreviations given refer to their base forms): the fully reduced leucoemeraldine (LEB), half-oxidized EB, and fully oxidized pernigraniline (PNB) form. The ES form—the only electrically conducting form of PANI—can be obtained either by protonation of EB or by oxidation of LEB. In Figure 3, the first redox couple at low potential and the second (partially irreversible) redox couple near 0.8 V represent the LEB–ES and the ES–PNB transition, respectively. The third minor redox couple at  $\sim 0.5$  V is associated with degradation products originating from the ES–PNB transition.<sup>44</sup> The thicknesses of the PANI(Cl) films polymerized on GC and TO are probably not the same. The TO/PANI(Cl) films were by purpose made thicker than the GC/PANI(Cl) films due to limitations in the sensitivity of the UV–visible spectrophotometer. This is reflected as a larger peak separation of the LEB–ES redox couple as can be seen in the CV of the TO/PANI(Cl) film. The higher peak separation indicates that the electrical conductivity is slightly lower for the films grown on TO than on GC.

The pH-dependent ES–EB transition of the TO/PANI(Cl) film is shown in Figure 4a. Characteristic absorbance maximums of the ES form (stable at low pH) can be observed in the spectra of PANI(Cl) at  $\sim 430 \text{ nm}$  and  $> 700 \text{ nm}$ , which are due to polaron band transitions ( $\pi$ – $\pi^*$ ).<sup>46</sup> The EB form (stable at high pH) has a characteristic absorbance maximum at 680–690 nm. The distortions observed in the spectra in Figure 4 at 380, 600, and 760 nm are caused by the spectrophotometer, which stops for a few seconds at these wavelengths before continuing the scan. The rather well defined isosbestic points indicate, however, that the ES form is converted directly to the EB form without any

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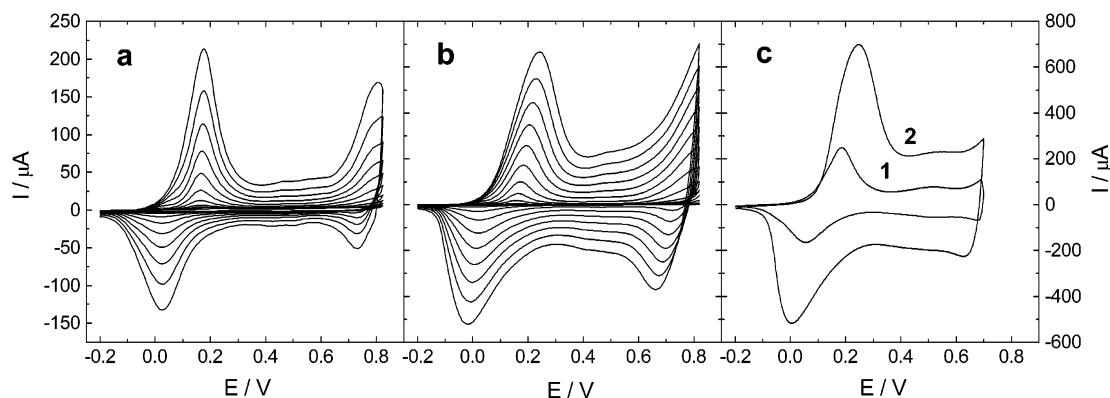


Figure 3. Polymerization of aniline in 1.0 M HCl on (a) GC (0.05 M aniline; 100 cycles, every 10th cycle shown), (b) TO (0.1 M aniline; 70 cycles, every 5th cycle shown), and (c) characterization of the obtained PANI(Cl) films in 1.0 M HCl: (1) GC/PANI(Cl) and (2) TO/PANI(Cl) ( $v = 50$  mV/s). The current scale is the same in (b) and (c).

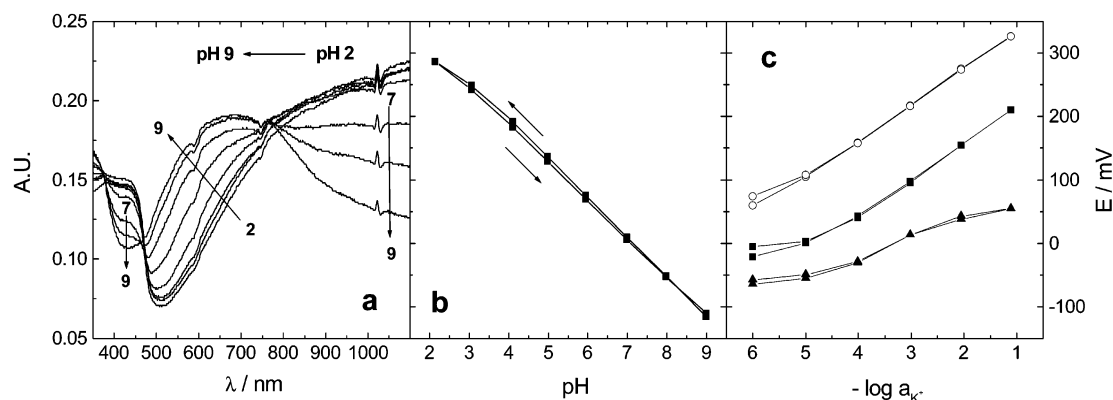


Figure 4. (a) UV–visible spectra of the TO/PANI(Cl) film measured from pH 2 to 9. (b) Potentiometric pH sensitivity of GC/PANI(Cl). (c) Potentiometric  $K^+$  sensitivity of solid contact electrodes prepared with the membrane type (containing the following additives): (■) M1 (valinomycin and KTpCIPB), (○) M2 (valinomycin), and (▲) M3 (no additives, only plasticized PVC). The potential scale is the same in (b) and (c).

intermediate oxidation states. Due to the strong pH sensitivity of PANI, potentiometric<sup>4,20,40,47–50</sup> and optical<sup>51–54</sup> pH sensors based on PANI have been reported in the literature.

Figure 4b shows the potentiometric pH sensitivity of GC/PANI(Cl). The PANI(Cl) electrodes show low hysteresis and a Nernstian slope of the calibration plot ( $59.0 \pm 1.0$  mV/pH). It must be pointed out that the pH response of PANI(Cl) is very selective because it was measured in pH buffer solutions with a high concentration of background electrolyte (see Experimental Section). It is also possible to measure the potential and UV–visible spectrum of the PANI(Cl) electrodes simultaneously (optopotentiometric measurements), which makes it possible to correlate potential changes with changes occurring in the UV–visible spectrum, i.e., structural changes of the PANI(Cl) film.<sup>40</sup> It was concluded based on previously reported optopotentiometric mea-

surements that the PANI(Cl) film was almost completely converted to the EB form at pH 9.<sup>40</sup>

**Solid Contact Electrodes.** The  $K^+$  sensitivity of the solid contact electrodes with the M1–M3 membranes is shown in Figure 4c. Almost Nernstian slopes of the calibration plots were observed for the M1 and M2 membranes ( $58.2 \pm 0.1$  and  $58.9 \pm 0.8$  mV/log  $a_K$ ) whereas the M3 membrane (only plasticized PVC) showed a highly sub-Nernstian slope with a rather high standard deviation and noisy electrode potentials. This is expected due to the absence of valinomycin ( $K^+$ -complexing ligand) and KTpCIPB in the electrode membrane resulting in a high bulk resistance of the plasticized PVC membrane.<sup>55</sup> The M1–M3 membrane types were chosen for this study in order to investigate the influence of KTpCIPB and valinomycin on the ES–EB transition of the inner PANI(Cl) solid contact layer.

The results of the potentiometric pH and  $CO_2$  sensitivity tests are shown in Figure 5. No pH sensitivity was observed for the solid contact electrode with the M1 membrane in a 1 mM KCl solution. It can therefore be concluded that the plasticized PVC membrane hinders the very pH sensitive ES–EB transition from occurring on short time scales although the pH of the test solution is changed. The potentials measured during the pH test are slightly higher than those shown in Figure 4c ( $10^{-3}$  M  $K^+$ ). This

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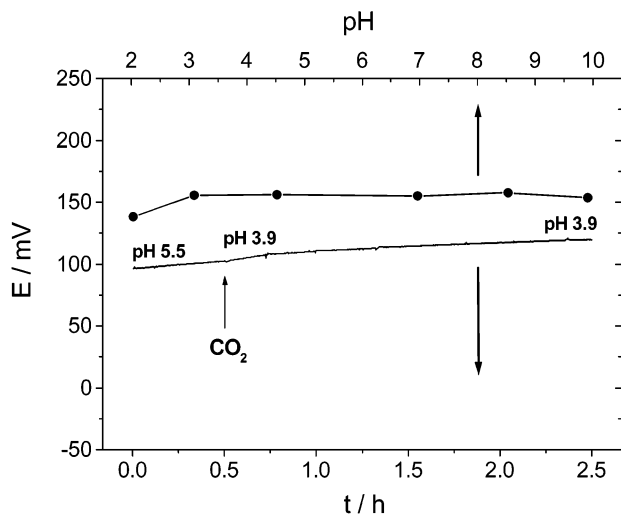


Figure 5. Potentiometric pH and  $\text{CO}_2$  sensitivity of the  $\text{K}^+$ -sensitive solid contact electrode prepared with the M1 membrane.

is due to the different ionic background used in these two studies. It should be noted that the potential at pH 2 was still slowly drifting toward higher values when the potential readings were taken.

The potential drift of the PANI-based solid contact electrodes was 8–9 mV/h during the  $\text{CO}_2$  sensitivity test (Figure 5). This is of the same magnitude that has been reported for PEDOT and much lower than for PPy, which is very surprising because the pH sensitivity of PANI should be much stronger than for PEDOT and PPy.<sup>31</sup> This discrepancy could, however, be explained with differences in the film thickness.

**UV–Visible Measurements.** The UV–visible spectra of the solid contact PANI(Cl) layers coated with the M1–M3 membranes are shown in Figure 6. They were equilibrated for 19 h in 1 mM KCl and buffer solutions with pH 6, 2, and 9, in the given sequence. The short-term stability of the PANI(Cl) solid contact is very good, and practically no changes in the characteristic UV–visible spectrum of the electrically conducting ES form can be observed even after keeping the membranes for 19 h at pH 9. The membrane types M1–M3 showed minor internal shifts in the absolute absorbance values, which are probably caused by variations in the background spectra. No influence of the film thickness of the M1 membrane on the stability of the PANI(Cl) film could be observed during the time scale of this experiment.

The thickness of the M1 membranes used in the UV–visible measurements shown in Figure 4a and d was approximately 250 and 60  $\mu\text{m}$ , respectively. The color of all PANI(Cl) films was dark green—characteristic of the ES form—after finishing the UV–visible measurement. The membranes were then stored in 1 mM KCl for the long-term stability test. pH-dependent changes taking place in the PANI(Cl) layer can also visually be observed because of the dark blue color of the EB form. Consequently, it can be concluded that the short-term stability of the PANI(Cl) solid contact layer is good between pH 2 and 9 independently of the membrane composition.

The long-term stability of the PANI(Cl) solid contact was studied in 1 mM KCl at pH  $\approx 5.5$  with the same electrode membranes that were used for the short-term stability test (Figure 7). The color of the solid contact PANI(Cl) layer of the M1 membrane was still green-blue after 93 days, typical for a mixed ES-EB form (Figure 7a), while the PANI(Cl) layers of the M2 and M3 membranes were dark blue already after 36 days in contact with the test solution (Figure 7b and c). This indicates a more complete ES to EB conversion of the PANI(Cl) layer of the solid contact electrodes prepared with the M2 and M3 membranes. The UV–visible spectrum of the PANI(Cl) layer of the M3 membrane measured after 43 days showing an absorbance maximum at  $\sim 700$  nm is characteristic of the EB form (Figure 7c). The UV–visible spectrum of the PANI(Cl) film coated with the M1 membrane taken after 93 days shows still, however, the characteristic absorbance maximum of the ES form at  $\sim 430$  nm, which has almost completely disappeared after 36 days for the PANI(Cl) films prepared with the M2 and M3 membranes. Figure 7b and c indicates that there are only minor time-dependent differences in the UV–visible spectra of these two membrane types.

The influence of the M1 membrane thickness on the stability of the inner PANI(Cl) layer was also studied (Figure 7a and d). Only minor changes occur during the first 16 days of the UV–visible spectrum of the PANI(Cl) film prepared with the thinner ( $\sim 60$   $\mu\text{m}$ ) M1 membrane. After 23 days, however, the absorbance maximum at  $\sim 430$  nm starts to decrease and minor changes of the green color of the PANI(Cl) layer can visually be observed (Figure 7d). No definite conclusions can be made based on these measurements concerning the difference in stability between the

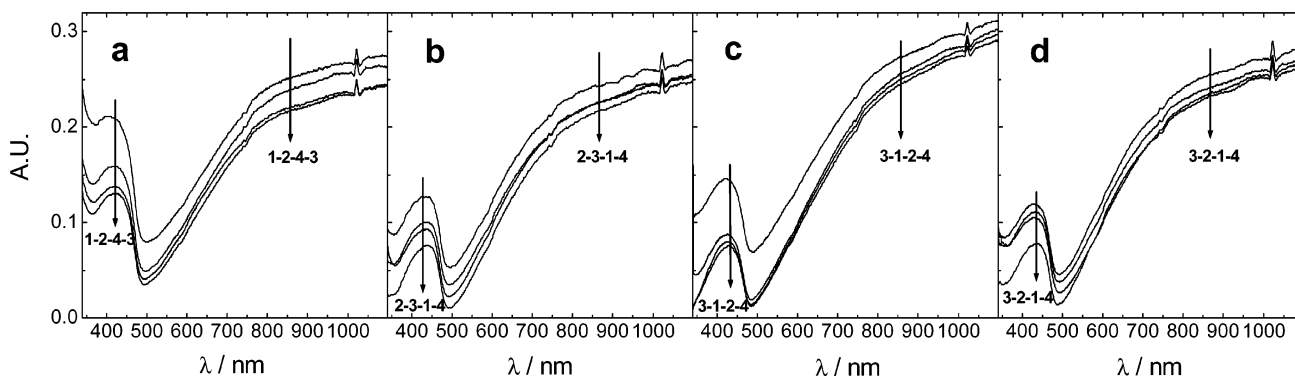


Figure 6. UV–visible spectra of the PANI(Cl) layer of  $\text{K}^+$ -sensitive solid contact electrodes prepared with the membrane type (containing the following additives): (a) and (d) M1 (valinomycin and KTpClPB), (b) M2 (valinomycin), and (c) M3 (no additives, only plasticized PVC). The spectra shown were measured after equilibration of the electrode membranes for 19 h at (1) pH  $\approx 5.5$  (1 mM KCl), (2) pH 6, (3) pH 2, and (4) pH 9. Thickness of the PVC membrane: (a)–(c), 250  $\mu\text{m}$ ; (d) 60  $\mu\text{m}$ .

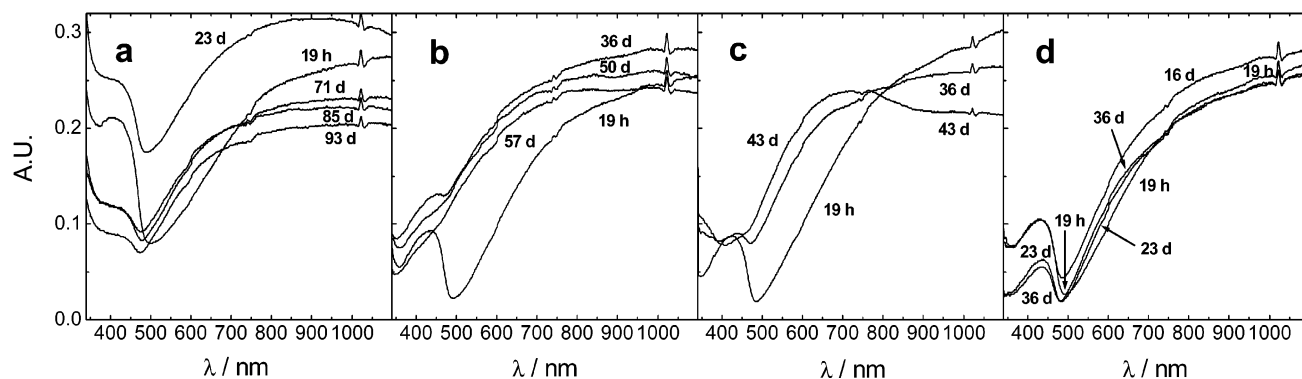


Figure 7. Long-term stability in 1 mM KCl (pH  $\approx$  5.5) of the PANI(Cl) layers of the  $K^+$ -sensitive solid contact electrodes. The ISMs have the same composition and thickness as the ISMs in Figure 6.

PANI(Cl) film prepared with the thinner and thicker ( $\sim 250 \mu\text{m}$ ) M1 membrane. It is, however, expected that on even longer time scales than shown in Figure 7, the PANI(Cl) film coated with the thinner PVC membrane should more easily be affected by solution pH than the PANI(Cl) film coated with the thicker membrane. It can be concluded that the PANI(Cl) solid contact layer of the thinner M1 membrane (Figure 7d) is much more stable than the PANI(Cl) layers of the electrodes prepared with the thicker M2 and M3 membranes (Figure 7b and c).

The reason for the higher instability of the PANI(Cl) layer, which is covered with the M2 and M3 membranes, is probably that the permselectivity of these membranes is lost (at least partially) due to Donnan failure when no negatively charged lipophilic additives (TpCIPB $^-$  ions) are present in the membrane phase.<sup>56</sup> It is therefore easier for the OH $^-$  ions to penetrate from the sample|ISM interface through the PVC membrane to the ISM|PANI(Cl) interface. This shows the additional importance of incorporating negatively charged additives to PANI-based solid contact ISEs in order to hinder or slow the ES–EB transition of PANI. The instability of the PANI(Cl) layer could eventually be counteracted by storing the electrodes between measurements at low pH because of the rather slow time-dependent changes occurring at the PANI(Cl) solid contact. This indicates that the diffusion of water and therefore also OH $^-$  through the plasticized PVC membrane is a rather slow process. The water uptake of plasticized ion-selective PVC membranes has, however, been studied more thoroughly by Harrison et al.<sup>57–60</sup> Another possibility to increase the stability of the PANI(Cl) layer could be to increase the amount of negatively charged lipophilic sites in the PVC membrane to hinder the diffusion of OH $^-$  through the membrane to the PANI(Cl) layer. The membrane compositions usually used for conventional ISEs with inner reference solution may therefore not always be directly transferred to all-solid-state solid contact ISEs. Other more lipophilic membrane matrixes than plasticized PVC should also be considered for PANI-based solid contact ISEs. It is also very important—especially in the case of PANI(Cl) due to its pronounced pH sensitivity—that the lipophilic additives do

not leach out from the membrane phase to the aqueous phase. The possibility that the PANI(Cl) layer possesses a certain pH buffer capacity should not be excluded because the PANI(Cl) layer was not washed with deionized water before the M1 membrane was applied on top of it after the conditioning step in 0.1 M HCl.

The method presented in this paper is universal and can be used to study the long-term stability of different types and combinations of CP-based solid contact materials (e.g., PPy and PEDOT) and plasticized PVC membranes. PANI can also be used as a model compound to study the diffusion of water to the ISM|PANI(Cl) interface of different types of PVC membranes or other membrane types, e.g., poly(methyl methacrylate), cellulose acetate, or polypropylene. The possibility of measuring the UV–visible spectrum and potential simultaneously has also recently been reported<sup>40</sup> and would eventually give more information about the reasons for the potential drifts of all-solid-state ISEs that have been reported in the literature. The pH-dependent color change of PANI provides an additional practically orientated tool for studying the stability of the inner solid contact layer. The influence of redox couples on the stability of the solid contact layer may as well be studied. It is also possible depending on the test conditions (low, middle, or high pH) to convert the PANI solid contact either to the electrically conducting ES form or the nonconducting EB form before the ISM is applied on the top of the PANI layer.

**Potential Stability Test.** The long-term potential stability of the  $K^+$ -selective solid contact electrode prepared with the M1 membrane was studied during 30 days in a 1 mM KCl solution with pH  $\approx$  5.5 (Figure 8). The electrode potentials were drifting continuously toward higher potentials during the first 10 days of the measurement. A potential drift is usually observed for PVC-based ISMs when in contact with the sample solution. This is probably due to equilibration processes taking place in the ISM phase and at the sample|ISM and the ISM|P interfaces. The increase in the potential during the 10 first days must be related to equilibration processes in the ISM phase or at the sample|ISM interface because no changes were observed in the UV–visible spectrum of the PANI(Cl) layer during this time period (Figure 7d). Conversion of the solid contact layer from the ES to the EB form (stability test carried out at pH  $\approx$  5.5) would result in a decrease of the electrode potential (Figure 4b), not an increase. The rather long equilibration time of  $\sim 10$  days can be due to the rather thick PVC membranes ( $\sim 400 \mu\text{m}$ ) that were used in the measurements. Also the charge-transfer processes taking place

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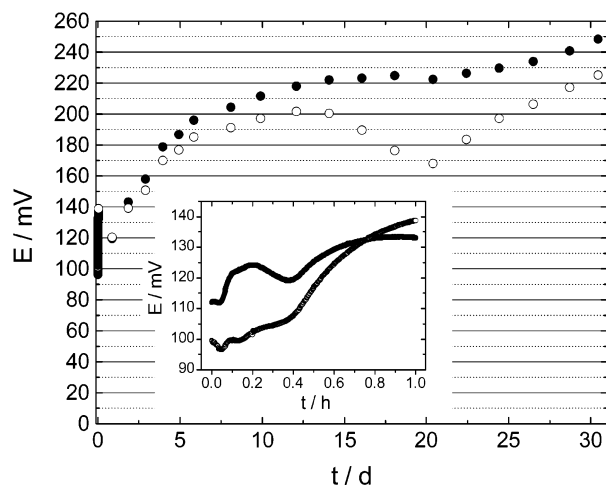


Figure 8. Potential stability measured in 1 mM KCl (pH  $\approx$  5.5) for two identical  $K^+$ -sensitive solid contact electrodes prepared with the M1-membrane. The inset shows the changes in the potential during the first hour of the electrodes in contact with the test solution.

at the ISM|PANI(Cl) interface have not yet been studied and are therefore not very well understood at the moment.

After  $\sim$ 15 days, one of the solid contact electrodes shown in Figure 8 started to show instability, which may indicate changes occurring at the ISM|PANI(Cl) interface. First the electrode potential decreased during approximately one week, which could be related to the ES–EB transition (see Figure 4b), and then increased again as can be seen in the figure (electrode potentials indicated with open circles). The exact reason for the instability of the electrode potential is unclear at the moment because it is difficult to relate changes in the electrode potential with a specific process taking place in the solid contact ISE. More information of changes occurring in the PANI(Cl) layer during the potentiometric measurements can be obtained by measuring the UV–visible spectra of the PANI(Cl) layer and the potential of the solid contact electrode simultaneously. This is possible with the optopotentiometric setup as reported recently.<sup>40</sup> It should also be noted that the instability of the electrode response might be caused by membrane components leaching out from the PVC membrane phase to the aqueous 1 mM KCl solution. The diffusion of the  $OH^-$  ions through the plasticized PVC membrane to the inner PANI(Cl) layer is facilitated especially if the concentration of KTpCIPB decreases in the membrane.

The second electrode shown in Figure 8 shows rather stable electrode potential (indicated with solid circles) after the initial potential drift of 10 days. The potential is, however, slightly drifting

toward higher potentials after  $\sim$ 25 days. The solid contact electrodes was calibrated after the stability test and showed a  $K^+$  sensitivity of  $50.9 \pm 5.1$  mV/log  $a_K$  ( $10^{-1}$ – $10^{-4}$  M KCl; i.e., 12.5% decrease in sensitivity).

## CONCLUSIONS

This paper presents a universal method based on UV–visible spectroscopy for determining the stability of the inner CP solid contact layer in all-solid-state ISEs. The method presented in this paper can be applied to various combinations of CPs and plasticized PVC membranes. The novelty of this method is based on the possibility of measuring the UV–visible absorbance spectrum of only the inner PANI layer of the solid contact electrode. It is reported that the  $K^+$ -sensitive solid contact electrodes prepared with PANI as the solid contact material had good short-term stability measured for 4 days in buffer solutions with pH 2–9 and a Nernstian slope of the calibration plot ( $58.2 \pm 0.1$  mV/log  $a_K$ ). It is concluded that on short time scales the PVC membrane effectively hinders the very pH sensitive ES–EB transition of the inner PANI layer.

The long-term measurements (1–3 months) showed instability of the PANI solid contact layer, and a partial conversion of the electrically conducting ES form to the nonconducting EB form was observed with UV–visible spectroscopy. The PANI solid contact layer coated with a PVC membrane containing negatively charged TpCIPB $^-$  anions was more stable at high pH than membranes without anionic additives. The diffusion of  $OH^-$  ions from the sample|ISM interface through the PVC membrane to the ISM|PANI(Cl) interface is probably facilitated due to the reduced permselectivity of the membranes containing no negatively charged additives. PANI can therefore be used as a model compound to study the diffusion of water from the solution|ISM interface to the ISM|P interface. ISMs with different membrane compositions than normally used in conventional ISEs may be required for all-solid-state solid contact ISEs in order to prevent instability due to protonation–deprotonation or oxidation–reduction processes occurring at the solid contact.

## ACKNOWLEDGMENT

This work is part of the activities of the Åbo Akademi Process Chemistry Centre within the Finnish Centre of Excellence Program (2000–2005) sponsored by the Academy of Finland.

Received for review April 13, 2004. Accepted May 26, 2004.

AC049439Q