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Potassium-Selective Electrodes with Stable and Geometrically Well-Defined Internal Solid Contact Based on Nanoparticles of Polyaniline and Plasticized Poly(vinyl chloride)

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Solid contact potassium-selective electrodes with the internal ion-to-electron transduction layer composed of plasticized poly(vinyl chloride) (PVC) and 2−20% (m/m) of polyaniline (PANI) nanoparticles, with the mean particle size of 8 nm, have been studied in this paper. UV−vis measurements in pH buffer solutions between pH 0 and 12 show that the electrically conducting emeraldine salt (ES) form of PANI has exceptionally good pH stability. Membranes of PANI nanoparticles were mainly in the ES form even at pH 12, in contrast to electrochemically prepared PANI(Cl) films, which are converted completely to the nonconducting form already at pH 6. Long-term UV−vis measurements with the PANI membranes in contact with aqueous buffer solution at pH 7.5 showed no degradation of the ES form. The PANI nanoparticles are homogenously mixed in the PVC-based solid contact (SC) layer. Only the uppermost part of the SC layer is to a minor extent dissolved in the outer potassium-selective PVC membrane. This enabled the preparation of geometrically well-defined inner SC layers, thus improving the reproducibility of the solid contact electrodes and resulting in good mechanical strength between the inner and outer membranes.

Polyaniline (PANI) is the most studied electrically conducting polymer (CP).[1] It can be prepared in a variety of different ways both electrochemically and chemically resulting in, for example, intractable thin films and soluble PANI, which can be processed together with commonly used bulk polymers. Stable dispersions of PANI in both aqueous and organic solvents were also recently prepared.[2−6] The processability of the soluble forms and dispersions of PANI is a useful property in practical applications, in comparison to many CPs, which are not processable. PANI is therefore still gaining much attention within the scientific community, almost 30 years since its rediscovery in late 1970s. Polymerization of aniline has been reported in ionic liquids[7−9] and in the presence of carbon nanotubes.[9,10] Lately, PANI has also been applied in organic electronics[11] and sulfonated PANI in organic diodes.[12]

One of the reasons for the interest in PANI is its very stable electrically conducting emeraldine salt (ES) form. The good environmental stability and the processability make PANI an attractive candidate for many applications. The chemistry of PANI is, however, slightly more complex than for most other CPs, due to the pH dependency of the three oxidation states of PANI.[1] Special care should therefore be taken when considering PANI for practical applications. It was recently reported that the protonation constant and pH of the half-transition point of the emeraldine base (EB) to ES transition ($pH_{1/2}$) could be used for describing the pH stability of PANI.[13] It was also shown that it was possible to tune the pH stability of PANI with the acid anion that was used in electropolymerization of aniline.[13,14] The pH stability of the ES form of PANI was extended to alkaline pH by performing the electropolymerization in 0.1 M dodecylbenzenesulfonic acid (bulky anion; $pH_{1/2} = 9.6$). In contrast, a less pH stable form of PANI was obtained with the $pH_{1/2}$ value of 6.1 when the electropolymerization was done in the presence of HCl.

The pH stability of PANI is of crucial importance when applying PANI as a component in all-solid-state ion-selective electrodes (ISEs). Surprisingly, the stability of the solid contact (SC) layer

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of PANI is reported in only one study,[15] although different types of electrochemically prepared[15−25] and soluble forms of PANI[26−34] have been applied as SC materials[15−25] and in the single-piece (SPE) configuration.[26−28,30−32] No stability studies have either been carried out with the other types of most commonly used CP-based SC materials, such as poly(pyrrole),[35] poly(3-octylthiophene) (POT),[36] and poly(3,4-ethylenedioxythiophene) (PEDOT). In most of the studies, it is only assumed that the CP-based SCs are stable, even though it is known that time-dependent changes of the oxidation state may occur within the CP phase. Most SCs based on PANI were electropolymerized from either aqueous solution of HCl or H_2SO_4. Water was therefore introduced to the SC layer already from the beginning of the electrode lifetime. In some cases, the PANI contact was washed with distilled water (pH $\cong$ 5.5−6.0) after the electropolymerization, which results in partial conversion of the conducting ES form to the nonconducting EB form.[22] In other words, optimization of the preparation procedure of all types of CP-based SC layers is still required in order to achieve a good piece-to-piece reproducibility of the electrodes. Different types of CP-based solid-state ISEs were recently reviewed by Bobacka.[37]

One possibility to improve the reproducibility of the standard potential of the solid contact electrodes, and to avoid the introduction of water to the SC layer already during the preparation procedure of the contact, is to use organic dispersions of CPs or CPs that are soluble in organic solvents; solid contact electrodes, based on both soluble PANI[29,30,33,34] and POT[34,38−43] and derivatives of POT,[44] have been reported. Also, an aqueous dispersion of PEDOT[45−48] and poly(3,4-dioctylthiophene) (PDOT),[49] which is soluble in chloroform, have been used in solid contact electrodes. In comparison to electrochemically polymerized CPs, the contacts prepared from soluble CPs or organic dispersions are usually easily soluble in the outer ion-selective membrane (ISM). This is the case with PANI dissolved with dodecylbenzenesulfonic acid (DBSA) and bis(2-ethylhexyl)phosphoric acid (DiOHP), PANI-(DiOHP)[50] (used in refs 29, 30, and 34), and POT,[41] which is soluble in most organic solvents. It is therefore difficult to prepare geometrically well-defined SCs in a reproducible manner. The use of DiOHP and DBSA as protonation agents for PANI is further limited by their water solubility. It can also be noted that the aqueous dispersion of PEDOT (Baytron P) is not stable in contact with water and must be stabilized by cross-linking with Ru-$(NH_3)_6^{3+}$, which is applied on the top of the PEDOT layer.[45] There are, however, no reports on the stability of the cross-linked PEDOT complex. It turns out that the construction of the solid contact electrode is technically not that trivial as can be expected at the first glance.

In this paper, the internal SC is prepared according to the SPE concept[26] by using an organic dispersion of PANI nanoparticles with a mean particle size of 8 nm. Similar concepts utilizing PANI-(DiOHP) and POT were quite recently introduced by Mihkelson et al.[29,30,34] and Maj-Żurawska et al.[33,39] In these concepts, the CP is dispersed within the plasticized PVC membrane. This work focuses on the long-term stability of PANI nanoparticles used in the internal SC, the preparation of geometrically well-defined contacts containing 2−20% (m/m) PANI, and the applicability of an organic PANI dispersion as a SC component.

EXPERIMENTAL SECTION

Chemicals. Valinomycin, potassium tetrakis(4-chlorophenyl)borate (KTpClPB), high molecular weight poly(vinyl chloride) (HMW PVC), and bis(2-ethylhexyl) sebacate (DOS) were obtained from Fluka. $K_4Fe(CN)_6$, $K_3Fe(CN)_6$, KH_2PO_4, and K_2HPO_4 were obtained from Merck.

PANI Dispersion. The PANI dispersion (D1003) with a mean particle size of 8 nm was obtained from Ormecon GmbH

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(Ammersbek, Germany). The size of 90% of the particles was <14 nm, and the conductivity in vacuum was given as 1.8×10^{-3} S/cm (spin-coated PANI films on ITO/glass substrate). The solid content of the green colored dispersion in xylene was 9.7% (m/m). The D1003 dispersion was stored in a closed glass bottle.

pH Buffer Solutions. The pH buffer solutions used for both potentiometric and UV−vis measurements were prepared according to Perrin et al.[51] and consisted of 25 mM citric acid (monohydrate) (≥99.5%), 25 mM Tris (p.a. ≥99.8%), 25 mM KCl (p.a.≥99.5%) (all from Fluka), 25 mM KH_2PO_4, and 25 mM $NaB_4O_7\cdot10H_2O$ (Merck). The pH buffer solutions were prepared with deionized water ($R = 18.2$ MΩ), and pH was adjusted with HCl or NaOH. Separate buffer solutions were prepared for each pH between 0 and 12.

Electrode Preparation. *Pure PANI Membranes.* Pure PANI membranes were prepared for impedance, conductivity, potentiometric, and UV−vis measurements by drop casting the organic PANI dispersion either on glassy carbon (GC) or tin oxide (TO) glass substrates. The experimental details are given below under the specific technique.

Solid Contact Electrodes. The K^+-selective membrane components were dissolved in cyclohexanon (CH) and mixed with 5 or 20% (m/m) of the PANI dispersion in xylene. SC layers were prepared by drop casting 5 μL of these solutions on GC substrates encapsulated in PVC bodies. The solvent was allowed to evaporate for 18 h before 20 μL of a tetrahydrofuran (THF) solution containing the components of the outer K^+-selective membrane (without PANI) was applied in five aliquots on the inner SC layer. The outer K^+-selective membrane was allowed to evaporate for 30 min before the next aliquot of the membrane solution was applied on top of the previous. The entire outer membrane was then allowed to evaporate overnight before the solid contact electrodes were conditioned in 0.1 M KCl, which was buffered to pH 7.5 with 10 mM phosphate buffer. The conventional K^+-selective membrane solution, which was used to prepare both the inner SC layers and outer membranes, had the following composition: 1.0% (m/m) valinomycin, 0.5% KTpClPB, 32.9% HMW PVC, and 65.6% DOS. The SC layers and the outer membranes were always cast from freshly prepared membrane solutions to avoid agglomeration of PANI particles.

Impedance Measurements. SC layers with 5, 10, and 20% (m/m) PANI were deposited for impedance measurements by drop casting of 20 μL of the membrane solutions on GC substrates encapsulated in PVC bodies. K^+-selective plasticized PVC membranes without PANI and PANI membranes without PVC and any other additives were prepared for comparison. The GC surfaces were cleaned first on a polishing cloth with 0.3-μm Al_2O_3 powder, rinsed with deionized water, and then polished again on a clean cloth. Finally, the GC electrodes were placed in ultrasonic bath for 20 min to remove traces of Al_2O_3. Before the impedance measurements, the electrode membranes were conditioned overnight in 0.1 M KCl, which was buffered to pH 7.5 with 10 mM phosphate buffer. The electrodes were then moved to a fresh solution with the same composition, and the impedance measurements were conducted in the frequency range of 100 kHz to 15
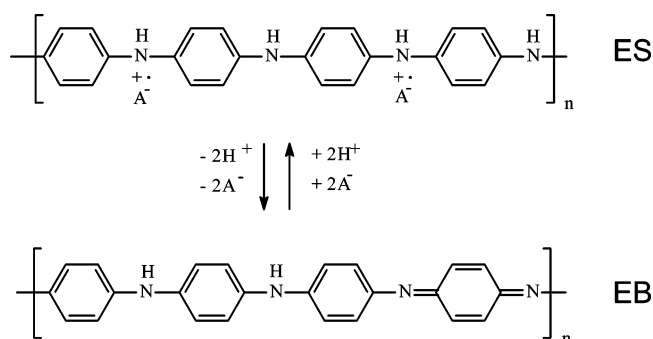
Figure 1. Reversible EB to ES transition of PANI.

mHz with a saturated calomel electrode (SCE) and a GC rod as the reference (RE) and counter electrode (CE), respectively.

Conductivity Measurements. SC layers with 2, 5, 10, 20, and 30% (m/m) PANI were deposited by drop casting of 10 μL of the membrane solutions on top of gold electrodes evaporated on microscope slide glass substrates. The area between the electrodes was 2×2 mm^2, and for simplicity, all current between the electrodes was assumed to be confined to this area. The conductivities of the films were estimated from current−voltage ($I-V$) measurements according to the method that was described earlier.[52] Film thicknesses were estimated to 40−70 μm using a micrometer. The conductivities were also measured for K^+-selective plasticized PVC membranes without PANI and PANI membranes without PVC and any other additives. The $I-V$ measurements were carried out with a Keithley 2612 source meter.

Potentiometric Measurements. *Redox Response.* The potentiometric redox response of pure PANI membranes was measured in 10 mM $Fe(CN)_6^{3-/4-}$ redox solutions with the [ox]/[red] ratio varying between 0.1 and 10. The redox solutions were buffered to pH 6 with 40 mM phosphate buffer in order to eliminate possible interferences from the pH-dependent EB−ES equilibrium (Figure 1). The solutions were stirred for 3 min, and the potential readings were taken after 2 min in quiescent solutions. The PANI membranes were prepared by drop casting of 10 μL of the PANI dispersion on GC substrates encapsulated in PVC bodies. The electrode membranes were allowed to evaporate for 5 h and were then conditioned overnight in 1.0 M HCl before the redox measurements. A SCE was used as the RE.

pH Response. The pH response was measured for pure PANI membranes, which were prepared and conditioned according to the same procedure as described above for the redox response. The pH response was determined in the pH buffer solutions described earlier (see Chemicals) with a SCE as the RE. The solutions were stirred for 3 min, and the potential readings were taken after 2 min in quiescent solutions.

Stability of the Potassium Response. The stability of the potassium response of the solid contact electrodes containing 5 and 20% PANI was studied during a period of 2 months with a SCE as the RE. The solid contact electrodes were calibrated once every week in $10^{-1}-10^{-6}$ M KCl solutions (23 $\pm$ 1 °C) without any background electrolyte. The calibration was done from low concentration to high and back to low. The solutions were stirred for 3 min, and the potential readings were taken after 2 min in quiescent solutions. Mean values of the potential readings obtained

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during this calibration sequence were used for calculation of the slope of the calibration graph. The potential readings were corrected for the liquid junction potential with Henderson's equation, and the activity coefficients were calculated with the Davies equation.[53]
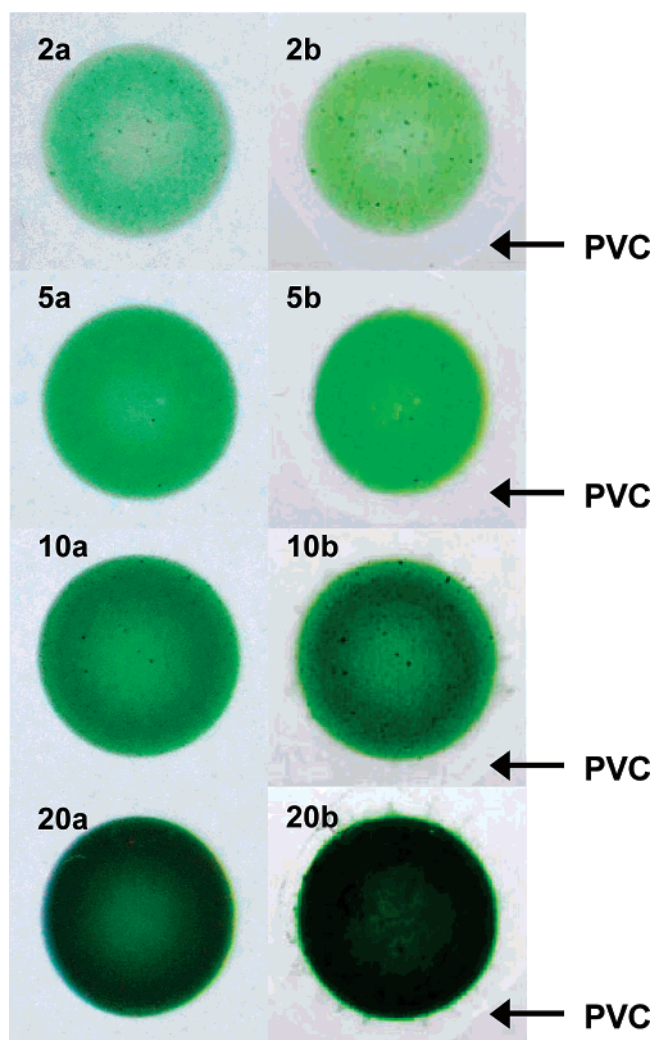
UV–Visible Measurements. The UV–vis spectra were measured between pH 0 and 12 for pure PANI membranes, which were deposited by solution casting of 5 μL of the PANI dispersion on TO glass substrates. The membranes were allowed to dry for 6 h before conditioning them overnight in 1.0 M HCl prior to the UV–vis measurements. The UV–vis spectra were determined after 20 min at equilibrium in the pH buffer solutions described earlier (see Chemicals). Time-dependent long-term changes of the UV–vis spectrum were studied in the buffer solution of pH 7.5. Between the measurements, the PANI membranes were stored in this solution. The background spectrum was always determined at pH 7.5 with two TO glass substrates placed in both the sample and reference light paths, respectively.

RESULTS AND DISCUSSION

Photos of the SC layers containing 2, 5, 10, and 20% PANI and the SC layers covered with the outer K⁺-selective plasticized PVC membranes are shown in Figure 2. The SC layers (photos to the left) were prepared on transparent microscope slides. PANI is dispersed homogenously in all SC membranes, although some aggregate of PANI can be observed especially in the membrane containing 2% PANI. It should be noted that the center of the membranes are thinner due to the solution casting technique. After deposition of the outer membrane (photos to the right), the SC layers still retain their original shape. Only the outermost parts of the SC layers containing 10 and 20% PANI are slightly dissolved in the outer membrane, thus improving the mechanical strength between the SC layer and the outer PVC membrane. It has been speculated, especially concerning electrochemically prepared SCs, that the interface between the SC and the outer membrane is not mechanically stable. This is possibly due to the water uptake and swelling of the outer PVC membrane, which may result in formation of water (or a layer of water) at this interface.[54]

One reason for the formation of two well-separated layers in the PANI-based solid contact electrodes was that the SC layers were prepared from CH solutions, which evaporate slowly. On the other hand, the outer K⁺-selective PVC membranes were deposited from THF solutions. THF evaporates quickly, and the contact time between THF and the SC layer could thus be minimized. The same combination of solvents was also recently used by Paciorek et al.[33] It should also be pointed out, that valinomycin (K⁺-selective ligand) is present in both the SC layer and the outer membrane, which makes the ion transfer reversible at this interface. The reversible charge transfer at the GC | SC interface is facilitated by PANI.

Impedance Measurements. The impedance measurements with SC layers containing 0, 5 and 20% PANI are shown in Figure 3. It is obvious that the capacitive contribution is considerably decreased by the addition of both 5 and 20% of PANI to the plasticized PVC membrane. It indicates that the charge transfer

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Figure 2. Photos of (a) the SC layers consisting of plasticized PVC containing 2, 5, 10, and 20% (m/m) PANI dispersion (membranes to the left, 2a–20a) and (b) the SC layers covered with an outer K⁺-selective plasticized PVC membrane without PANI (membranes to the right, 2b–20b). The photos were taken with a digital camera.

at the GC | SC interface is improved by PANI. This was also observed previously with Ca²⁺-selective SPEs.[27] The bulk impedance of the SC layers in this work is not, however, affected by PANI. The bulk resistance was ~800 kΩ for all membranes shown in Figure 3. The ionic conductivity of the SC layers with 0, 5 and 20% PANI was estimated from the bulk resistance to 3×10^{-9}–9×10^{-8} S/cm by assuming a membrane thickness of 20–50 μm and a membrane diameter of 0.15–0.5 cm.
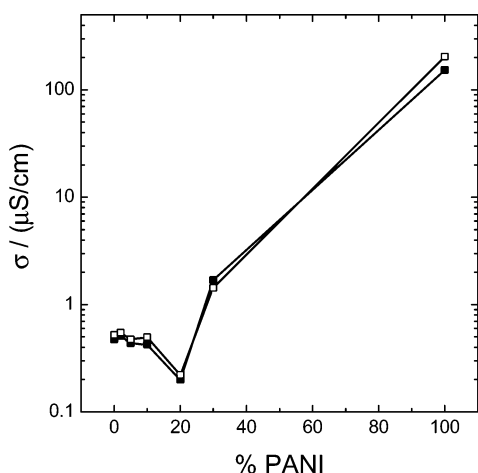
Conductivity Measurements. The conductivities of SC layers containing different amounts of PANI are shown in Figure 4. The conductivities of the SC membranes are practically constant between 0 and 10% PANI but decrease slightly between 10 and 20% PANI. On the other hand, the conductivity was observed to increase ~1 order of magnitude between 20 and 30% PANI. The reason for the almost constant conductivity of the membranes containing 0–20% PANI is probably that the PANI nanoparticles act as electrically conducting filler particles in the electrically nonconducting PVC matrix. According to the classical conduction theory, ~17% of electrically conducting spherical filler particles are usually required to reach the percolation threshold and turn on the electrical conductivity of nonconducting bulk materials.
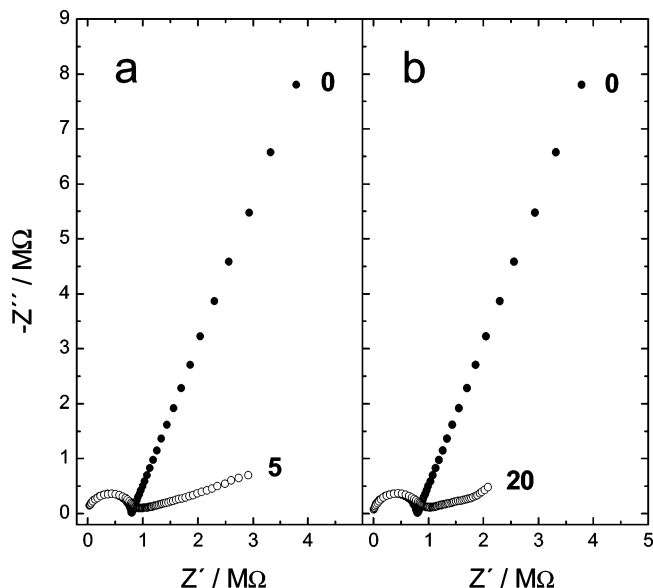
Figure 3. Impedance spectra of the coated wire electrode (CWE; solid circles; a and b) and the electrodes consisting only of the SC layers prepared with 5% PANI (open circles, a) and 20% PANI (open circles, b). $f = 100$ kHz-15 mHz; $\Delta E = 0.1$ V (CWE), and $\Delta E = 10$ mV (SC layers).

Figure 4. Conductivity (σ) of SC layers of plasticized PVC membranes containing different amounts of PANI dispersion. Two different sets of membranes were measured.

The percolation threshold is, however, dependent on the geometry and size of the conducting filler particles.[55] The conductivity of the SC membranes containing 0–20% PANI is thus probably governed mainly by the ionic conductivity. The conductivity of the PVC membrane without PANI (0%) was estimated to 5×10^{-7} S/cm (Figure 4). This value is in acceptable accordance with the estimation of the ionic conductivity obtained from the impedance measurements. At PANI concentrations of >20%, a conducting network is probably formed within the PVC membrane and the conductivity is thus to a great extent controlled by the electrical conductivity of the PANI nanoparticles. It was previously reported that the addition of very low concentrations of soluble PANI-(DiOHP) (e.g., 0.4% (m/m)) could increase the electrical conductivity of a nonconducting cellulose acetate matrix by several orders
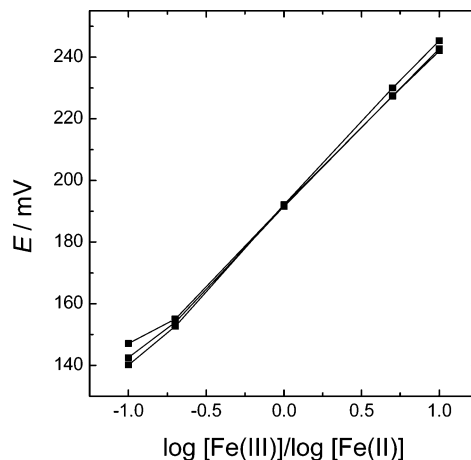
Figure 5. Redox response of pure PANI membranes ($n = 3$).

of magnitude.[56] In this case, the low concentration of PANI that is required to turn on the electrical conductivity is due to phase separation between PANI(DiOHP) and cellulose acetate.

It is most important that PANI is present at the GC | SC interface to improve the charge transfer at this interface. It is, in fact, not desirable to form an electrically conducting pathway within the SC membrane due to the characteristic redox sensitivity of the CPs. The electrical conductivity of the pure PANI membranes (100%) was estimated to 2×10^{-4} S/cm (Figure 4). This value is also in rather good accordance with the conductivity values reported by Ormecon GmbH. It should be noted, that it is assumed that the surface and bulk conductivities of all SC membranes are the same due to homogenously dispersed PANI within the PVC membrane.

Redox Response. The redox sensitivity of the pure PANI membranes was studied in Fe(CN)$_6^{3-/4-}$ solutions with [ox]/[red] varying between 0.1 and 10 (Figure 5). The redox response of 51.1 ± 2.3 ($n = 3$) mV/decade was slightly lower than the theoretically slope of ∼60 mV/decade. This is probably due to the semiconducting nature of the PANI dispersion. It was also observed that the redox response was quite sluggish, which can be seen in Figure 5 for [ox]/[red] = 0.1. The redox activity shows, however, that PANI can be oxidized and reduced, thus facilitating the charge transfer at the GC | SC interface. The presence of PANI at the GC | SC interface ensures that charge transfer occur at this interface (cp. with impedance measurements), even though a continuous network of PANI is not formed in the solid contact electrodes containing 5 and 20% PANI.

UV–Vis Measurements. The UV–vis spectra of the pure PANI membrane measured between pH 0 and 12 are shown in Figure 6a. The results indicate that the ES form of the PANI membranes has exceptionally good pH stability between pH 0 and 9, and even at pH 12, most of the film is still in the ES form. Most types of PANI membranes have usually converted to the EB form at pH 9 (Figure 1). The UV–visible spectrum recorded at pH 0–9 is characteristic of the ES form with absorbance maximums at ∼430 and 750–780 nm, which are associated with polaron band transitions.[57] The absorbance maximum at 750–780 nm indicates that the charge distribution is partially localized in the PANI

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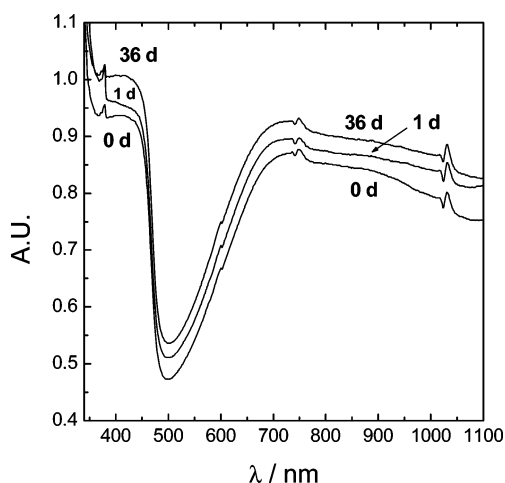
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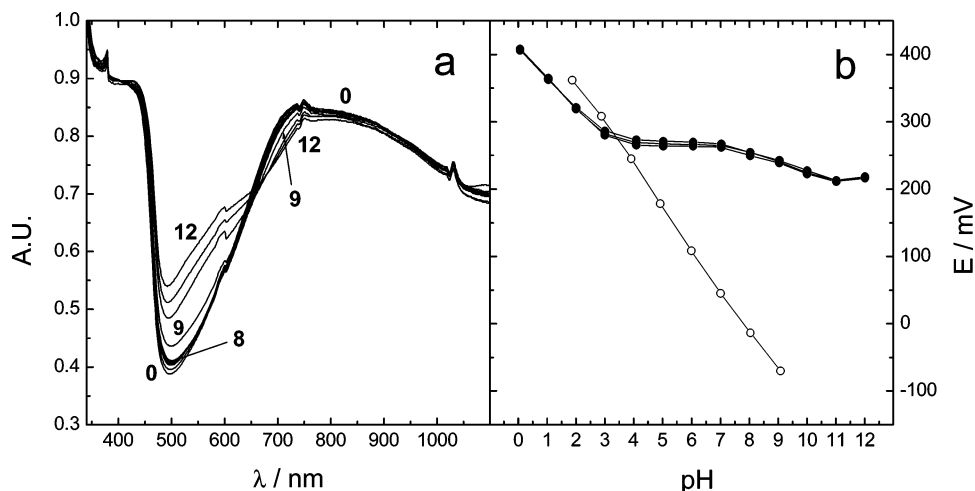
Figure 6. (a) UV−vis spectra and (b) the potentiometric pH sensitivity of pure PANI membranes measured between pH 0 and 12. For comparison, the potentiometric pH sensitivity of the PANI(Cl) membrane (open circles) is shown in (b).

Figure 7. Long-term UV−vis stability test of the pure PANI membrane at pH 7.5. The UV−vis spectrum was measured immediately after placing the film in the buffer solution (0 d) and after 1 day (1 d) and 36 days (36 d) in contact with the solution.

nanoparticles.[58] The nonconducting EB form has an absorbance maximum at ∼600 nm.[52,59] The minor peaks observed in the spectra at 380, 600, and 750 nm are caused by the photometer, which stops the wavelength scan for a few seconds at these wavelengths.

The pH stability of the ES form of pure PANI membranes was studied in a buffer solution at pH 7.5 (Figure 7). The stability study was conducted over a period of ∼1 month (36 days), and the UV−vis spectra in Figure 7 show that no degradation of the ES form takes place during this period. It can therefore be assumed that the PANI nanoparticles dispersed in the SC membranes have good pH stability. However, after ∼40 days of the stability test, the entire PANI membranes fell off from the TO substrate as one piece. This was most probably due to poor long-term adhesion of the PANI membrane to the TO substrate.

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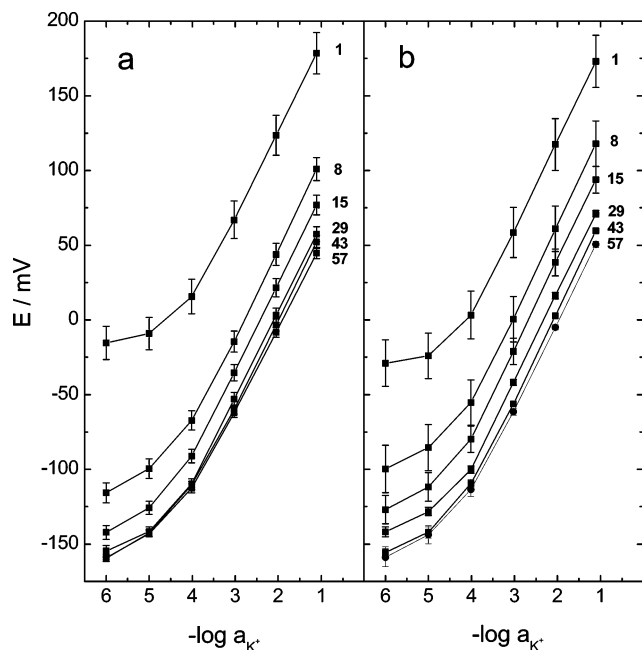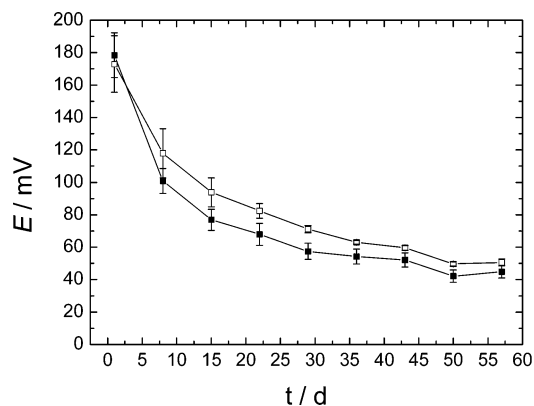
of the pure PANI membranes is shown in Figure 6b. Practically no pH response was observed between pH 4 and 7. A highly suppressed pH response of only ∼13 mV/decade was observed between pH 8 and 11. On the other hand, the pH response was rather pronounced with a slope of ∼44 mV/decade between pH 0 and 3. This is due to further protonation of the PANI nanoparticles. The pH stability of solid contact electrodes prepared with a SC layer of electrochemically prepared PANI(Cl) was recently reported.[15] For comparison, the pH response of 62.4 ± 0.9 mV/ pH (n = 3) of PANI(Cl) is therefore also shown in Figure 6b.[14] It is clear that there is a remarkable difference in the pH response of electropolymerized PANI(Cl) films and membranes prepared of PANI nanoparticles. It is also obvious that the latter membrane type is more suited as an SC layer due to its high pH stability between pH 4 and 7. It was previously shown that the long-term stability of PANI(Cl) was poor in different types of PVC-based solid contact electrodes and that a partial conversion of the ES to EB form took place during the stability study at pH 5.5.

The long-term stability of the K+ response of solid contact electrodes with SC layers containing 5 and 20% PANI was studied in aqueous solutions of $10^{-1}-10^{-6}$ M KCl over a period of 2 months (Figure 8). The results in Table 1 show that practically no degradation of the potentiometric K+ response is observed during the first month. After 57 days, the slope has decreased with 3.4% for both the solid contact electrode containing 5 and 20% PANI, respectively, in comparison to the slopes determined during the first day of the stability study (Table 1). The decrease of the potentiometric slope can be associated with leaching of membrane components (mainly KTpClPB and valinomycin) from the membrane to the solution phase. The solid contact electrodes consisting of 20% PANI show slightly better slopes and lower standard deviations than the electrodes prepared with 5% PANI. This possibly indicates that higher PANI concentration in the SC layer is advantageous for the charge transfer at the GC | SC interface.

The potential stabilities of the solid contact electrodes in 0.1 M KCl are shown in Figure 9. The stability curves were constructed by using the potentials that were measured in 0.1 M KCl during the long-term stability study of the K+ response (Figure

Figure 8. Calibration graphs of the solid contact electrodes prepared with (a) 5 and (b) 20% PANI measured in $10^{-1}-10^{-6}$ M KCl without any background electrolyte ($n = 3$). The graphs were obtained during a period of 2 months (57 days). The days when the calibrations were done are given by the numbers to the right in the figures.

Table 1. Potentiometric K$^+$ Responses of Solid Contact Electrodes ($n = 3$) over a Period of 2 Months^a

	slope (mV/decade)	
day	5% PANI	20% PANI
1	56.3 ± 0.8	58.8 ± 0.5
8	58.2 ± 0.5	60.0 ± 0.0
15	58.0 ± 0.7	60.0 ± 0.0
22	56.6 ± 0.8	58.6 ± 0.5
29	57.7 ± 0.5	59.1 ± 0.3
36	56.1 ± 1.0	57.9 ± 0.4
43	56.2 ± 0.9	58.5 ± 0.5
50	55.6 ± 0.7	57.2 ± 0.3
57	54.4 ± 1.2	56.8 ± 0.8

^{a} The slopes were calculated in the concentration range of $10^{-1}-10^{-4}$ M KCl.

Figure 9. Long-term potential stability of the solid contact electrodes in 0.1 M KCl. The SCEs were prepared with 5 (solid squares) and 20% PANI (open squares).

with penetration of water to the GC | SC interface. Further studies are, however, required to evaluate this possibility. Approximation of the contact angles between a droplet of water and the pure PANI membrane (~40°), and the PVC membranes dissolved in THF (~80°) and CH (~80°), show that the PANI membrane is more hydrophilic than the PVC membranes. The addition of PANI in the PVC membrane may therefore facilitate the water uptake of the SC contact, which is a drawback of the solid contact electrode concept proposed in this paper.

CONCLUSIONS

It is shown that K$^+$-selective solid contact electrodes with stable SC layers consisting of PANI nanoparticles and plasticized PVC can be prepared. In contrast to electrochemically prepared PANI (in HCl),[15] the pure PANI membranes with exceptionally good pH stability do not show any degradation of the conducting ES form at pH 7.5 during a period of 1 month. PANI nanoparticles can therefore be applied as a membrane component in solid contact electrodes.

The outermost parts of the SC layers are only slightly dissolved in the outer PVC membrane, which results in geometrically well-defined SCs with good mechanical strength of the SC | ISM interface. Impedance measurements revealed that PANI lowers the capacitive contribution at the GC | SC interface, thus improving the charge transfer at this interface. Conductivity measurements indicate that no continuous network of PANI, which could make the SC membrane sensitive to redox couples, was formed within the SC layers when the PANI concentration was ≤20%. The Nernstian K$^+$ response of the solid contact electrodes prepared with 5 and 20% PANI was practically constant during the first month of use and showed only minor degradation during a period of 2 months.

8). The potential stability curves in Figure 9 reveal that the potential drift is highest during the first week of the stability study. It is well-known that water uptake of plasticized PVC membranes is most pronounced during the first weeks in contact with aqueous solution. A much lower potential drift is observed when the electrode lifetime exceeds 2 weeks. The initial potential drift of the solid contact electrodes can be therefore probably related to the water uptake of the outer PVC membranes and PVC part of the SC layer and not to instability of the PANI nanoparticles in the SC layer (Figure 7). The potential drift is slightly lower for the solid contact electrodes with 20% PANI. On the other hand, the standard deviations of the potential readings are higher for these electrodes during the first two weeks of the stability study, in comparison with the solid contact electrodes containing 5% PANI. The potential readings of the solid contact electrodes with 20% PANI become very reproducible after 2 weeks in contact with 0.1 M KCl. The potential drift and the increased reproducibility of the standard potential with time may possibly be connected