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Pre-Polarized Hydrophobic Conducting Polymer Solid-Contact Ion-Selective Electrodes with Improved Potential Reproducibility

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ABSTRACT

Electrically conducting polymers (ECPs) are one of the most popular types of materials to interface ion-selective membranes (ISM) with electron conducting substrates to construct solid contact ion-selective electrodes (SCISEs). For optimal ion-to-electron transduction and potential stability, the p-doped ECPs with low oxidation potentials such as PPy need to be generally in their conducting form along with providing a sufficiently hydrophobic interface to counteract the aqueous layer formation. The first criterion requires that the ECPs are in their oxidized state, but the high charge density of this state is detrimental for the prevention of the aqueous layer formation. We offer here a solution to this paradox by implementing a highly hydrophobic perfluorinated anion (perfluorooctane sulfonate, PFOS⁻) as doping ion by

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3 which the oxidized form of the ECP becomes hydrophobic. The proof of concept is shown by
4 using polypyrrole (PPy) films doped with PFOS⁻ (PPy-PFOS) as the solid contact in K⁺-
5 selective SCISEs (K⁺-SCISE). Prior to applying the plasticized poly(vinyl chloride) ISM, the
6 oxidation state of the electrodeposited PPy-PFOS was adjusted by polarization to the known
7 open circuit potential of the solid contact in 0.1 M KCl. We show that the pre-polarization
8 results in a hydrophobic PPy-PFOS film with a water contact angle of 97±5°, which
9 effectively prevents the aqueous layer formation under the ISM. Under optimal conditions the
10 K⁺-SCISEs had a very low standard deviation of E^0 of only 501.0±0.7 mV that is the best E^0
11 reproducibility reported for ECP-based SCISEs.
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27 Keywords: electrically conducting polymer, perfluorinated dopant anion, solid contact ion-
28 selective electrode, potassium ion, pre-polarization
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34 Introduction section

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36 Ion-selective electrodes (ISEs) are established analytical tools in volumetric, clinical and
37 environmental analysis and process control.¹⁻⁴ However, the cost-effectiveness, ease of use,
38 and monitoring capabilities of ISEs, as well as their excellent accuracy demonstrated in the
39 clinical analysis of blood electrolytes would make them suitable for an even wider range of
40 applications. The use of ISEs in potentiometric bioassays,⁵⁻⁹ portable paper based platforms¹⁰⁻
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12 as well as wearable sensors^{13,14} are relevant examples of emerging applications. However,
the single-use disposable ISEs generally required by these applications would benefit from a
rugged and cost-effective miniaturized electrode design that is compatible with mass
production technologies.¹⁵⁻¹⁷ In this respect, the replacement of the liquid inner filling solution
of conventional ISEs with a solid contact (SC) layer that interfaces the electron conducting

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3 substrate and the ion selective membrane (ISM) emerges as a major enabling technology.¹⁸⁻²¹
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5 The role of the SC is to provide a stable inner phase boundary potential^{20,22,23} at the
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7 substrate/SC and SC/ISM interfaces, and to prevent the aqueous layer formation at the inner
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9 interface, which coupled to diffusion of ionic species within the ISM may lead to potential
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11 instability.²⁴ As all ISMs exhibit water uptake²⁵⁻³¹, the prevention of the aqueous layer
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13 formation^{32,33} with ill-defined ion activity has proven to be a major challenge.
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20 The mainstream of the SCISE research is based on electrically conducting polymers (ECPs)³⁴⁻
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22 ³⁶, large surface area carbon materials^{32,37-40} and their (nano)composites⁴¹⁻⁴³, but also many
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24 other important types of SC materials have been reported such as redox polymers⁴⁴, electron-
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26 ion exchange resins⁴⁵, redox-active self-assembled monolayers³², tetrakis(4-
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28 chlorophenyl)borate anion doped nanocluster films⁴⁶, nanoporous Au films⁴⁷, and three-
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30 dimensional molybdenum sulfide nanoflowers.⁴⁸ SCISEs with adequate potential stability
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32 were reported for both the ECP and carbon materials, but the use of large surface area inert
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34 carbon materials apparently results in better potential stabilities and less susceptibility to
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36 environmental conditions.^{37,39} In turn, ECPs have an essential advantage in terms of
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38 controlled local deposition by electropolymerization aiding the miniaturization and mass
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40 fabrication of SCISEs.⁴⁹⁻⁵¹ However, they show a larger degree of complexity both due to the
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42 diversity of the ECPs and doping ions as well as due to the mechanism of the stabilization of
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44 the inner phase boundary potential. Generally, a mixed ionic and electronic conduction is
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46 required for this purpose that is best achieved in the conducting state of the ECP, *i.e.* in its
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48 oxidized form. While this form is usually the most stable it also induces a larger charge
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50 density on the polymeric backbone that is compensated during synthesis by incorporation of
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52 charge compensating counter ions. The increased charge density, however, commonly
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3 increases the hydrophilicity of the film making it difficult to prevent the aqueous layer
4 formation even for highly hydrophobic ECPs, raising also adhesion problems.
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10 Here we have addressed this paradox of ECP-based SCISEs by incorporating a highly
11 hydrophobic anion, perfluorooctane sulfonate (PFOS⁻), as the charge compensating (doping)
12 anion in the polypyrrole (PPy) solid-contact film during its electrochemical synthesis. Unlike
13 the tetraphenyl borate derivatives, the PFOS⁻ has besides its hydrophobicity also excellent
14 chemical stability. Electrowetting studies⁵² previously demonstrated that such PPy-PFOS
15 layers can be made superhydrophobic in their oxidized state due to large amount of PFOS
16 anions incorporated in the polymeric matrix. Thus in contrary to most ECPs, such films are in
17 fact more hydrophobic in the oxidized state than in the reduced state.⁵² To ensure the
18 maximum hydrophobicity and stability of the PPy-PFOS solid-contact, we have pre-polarized
19 the SC⁵³ before covering it with the ISM to adjust the PPy-PFOS film to its stable oxidized
20 and hydrophobic form. By this procedure we expected to improve also the reproducibility of
21 the standard potential (E^0), as the large deviation of E^0 is a common problem of SCISEs. If
22 unsolved, each electrode needs to be calibrated individually for direct potentiometry that is
23 cumbersome, and constitutes a major limitation for development of single-use disposable
24 SCISEs. Small variations in the initial oxidation state and composition of the ECP layer are
25 factors affecting the potential reproducibility of the ECP-based solid-contacts. It is therefore
26 expected that the adjustment of the oxidized form of the ECP should minimize this problem.
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28 Indeed, recently it was shown that the standard potential of ECP-based SCISEs can be
29 adjusted by polarizing or short cutting the respective SCISEs against a reference electrode.⁵⁴
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31 However, the potentials of the SCISE are usually drifting after these treatments and the
32 reproducibility of the standard potential lags much behind the state of the art SCISEs having
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3 redox buffer⁵⁵ and graphene/carbon black-fluorinated acrylic copolymers⁴² as SC with
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5 standard deviations (SD) in the best case as low as 0.7 mV and 0.1 mV, respectively.
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10 We report here that the pre-polarization of the SC is a much more efficient way to ensure the
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12 reproducibility of the standard potential and for the PPy-PFOS based K⁺-selective SCISEs. In
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14 the best case, it results in the smallest SD of 0.7 mV reported up to now for ECP-based
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16 SCISEs.
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20 21 22 **Experimental section**

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24 **Chemicals.** FeCl₃·6 H₂O, acetonitrile (ACN, 99.5%, anhydrous), KCl and
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26 heptadecafluorooctanesulfonic acid tetraethylammonium salt (TEAPFOS, Et₄N⁺SO₃⁻
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28 CF₂(CF₂)₆CF₃, 98%) were received from Sigma-Aldrich and used without additional
29
30 purification. Pyrrole was also purchased from Sigma-Aldrich and distilled prior to use. High
31
32 molecular weight PVC (HMW PVC), bis(2-ethylhexyl) sebacate (DOS), potassium
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34 tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (KTFPB), potassium ionophore I (valinomycin),
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36 and tetrahydrofuran (THF), all Selectophore grade, were purchased from Fluka and used as
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38 received. Deionized water (ELGA, 18.2 MΩ) was used to prepare the aqueous solutions.
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46 **Electrosynthesis and pre-polarization of the PPy solid contact.** Pyrrole was polymerized
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48 with a combined electrochemical and chemical polymerization method from an ACN solution
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50 containing 0.1 M pyrrole, 0.05 M TEAPFOS and 2.0×10⁻⁴ M FeCl₃·6 H₂O.^{52,56} Prior to the
51
52 polymerization, the glassy carbon (GC) electrodes were first polished with 0.05 μm Al₂O₃
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54 suspension, then on a clean polishing cloth and finally rinsed with deionized water and ACN.
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56 In the three-electrode cell, the GC electrodes (incorporated in PEEK bodies), the coiled Pt
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3 wire and the Ag/AgCl wire served as the working, counter and reference electrodes
4 (calibrated vs. ferrocene/ferrocenium), respectively. All freshly prepared solutions (V=3 ml)
5
6 used for the synthesis and pre-polarization of the PPy films were purged with nitrogen gas for
7
8 5 min before the experiments. The chemical polymerization of pyrrole was first initiated for
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10 ca. 15 min by adding $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ to the pyrrole-TEAPFOS-ACN solution that was expected
11
12 to facilitate the electropolymerization and promote the formation of a rougher and more
13
14 hydrophobic PPy film surface.⁵² The electropolymerization was then carried out
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16 galvanostatically for 15 min at 0.25 mA cm^{-2} (controlled by the Autolab PGSTAT 12 or
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18 PGSTAT 30 potentiostats) in a three-electrode one-compartment cell on GC electrodes (d=1.6
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20 mm). After the polymerization, the formed PPy films were characterized by cyclic
21
22 voltammetry (CV) in monomer- and chloride-free 0.05 M TEAPFOS-ACN electrolyte
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24 solution in the three-electrode cell described above and then pre-polarized at 0.18 V in this
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26 solution for 10 min before rinsing the films with ACN. Finally, the PPy films were dried in
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28 ambient air for 5 min prior to the ISM casting.
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39 **Fabrication of the K^+ -SCISEs.** The ISM cocktail solutions were prepared by adding totally
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41 100 mg of the following membrane components into 1 ml THF: 32.9 % (w/w) HMW PVC,
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43 65.7% DOS, 1.0 % valinomycin, and 0.4 % KTFPB. After the polymerization, pre-
44
45 polarization and drying of the PPy films, 40 μl of the ISM cocktail solution was deposited
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47 onto the PPy films in three aliquots of 15 μl , 15 μl and 10 μl covering the whole electrode
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49 surface and resulting in the ISM thickness of ca. 150 μm . The three-step drop casting
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51 procedure prevented the pinhole formation in the ISM.⁵¹ The K^+ -SCISEs were allowed to dry
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53 overnight in ambient atmosphere prior to use.
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3 **Characterization of the water contact angle and morphology of the solid contact.** The
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5 water contact angles (WCAs) were measured with a CAM200 goniometer (KSV Instruments
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7 Ltd., Helsinki, Finland) and the static CA was determined after 10 s of applying the water
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9 droplet (2 μL) on the PPy film surface. The surface morphology and the thickness of the PPy
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11 films were analyzed with scanning electron microscopy (SEM; LEO 1530 Gemini FEGSEM
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13 instrument). The PPy films for the WCA and SEM measurements were prepared on Pt
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15 sputtered ITO glass.
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22 **Water uptake of the PPy-PFOS solid contact.** The water uptake of the PPy-PFOS film
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24 deposited on a Pt sputtered ZnSe reflection element was determined with Fourier transform
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26 infrared attenuated total reflectance (FTIR-ATR) technique using the previously reported
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28 experimental setup.^{29,31,57} The electropolymerization of the PPy-PFOS film on ZnSe is
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30 described in the Supporting Information. Briefly, the sample compartment of the FTIR
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32 instrument was purged with dry air for 30 min before starting the water uptake measurements
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34 of the PPy-PFOS film. The background spectrum and the first FTIR spectrum in the
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36 measurement sequence were recorded without any electrolyte in the cell. After measuring the
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38 first spectrum (a straight line) the cell was quickly filled with deionized water and the FTIR
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40 spectra were then measured once every minute for the first 2 h and with 15 min intervals
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42 during the next 22 h. The FTIR measurements were done with a Bruker IFS 66/S
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44 spectrometer equipped with a DTGS detector. Twenty-five interferograms were recorded for
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46 each spectrum measured with the resolution of 4 cm^{-1} and the gain factor of 64. The
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48 penetration depth (d_p) of the evanescent wave was estimated with the Harrick equation⁵⁸ to be
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50 ca. 0.5-0.6 μm and ca. 1.1-1.3 μm in the wavenumber regions of 3000-3700 cm^{-1} (OH
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52 stretching vibrations of water)^{59,60} and 1500-1800 cm^{-1} (H-O-H bending vibrations)⁶¹,
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3 respectively, by assuming that the $n_{\text{ZnSe}}=2.430-2.435$ and $n_{\text{PPy}}=1.5$.⁶² However, the penetration
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5 depths can be influence to some extent by the 30 nm thick sputtered Pt layer that covers the
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7 ZnSe surface. The mathematical modelling of the water diffusion coefficients from the water
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9 uptake spectra is described in the Supporting Information.
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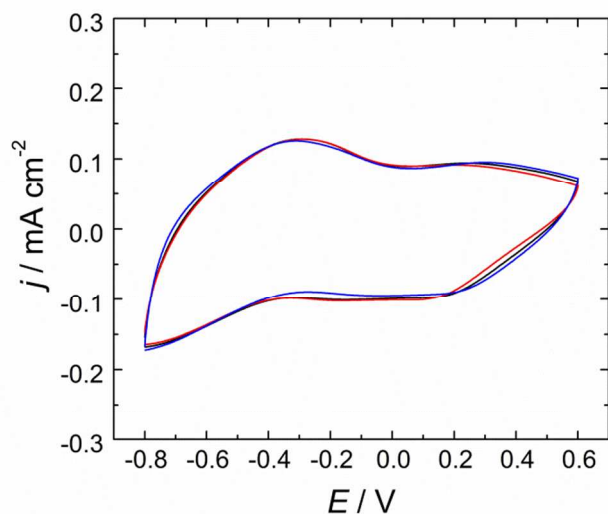
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15 *In situ* FTIR-ATR spectra of the PPy-PFOS film prepared on the Pt sputtered ZnSe were also
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17 recorded at different applied potentials in the spectroelectrochemical cell in the presence of
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19 0.05 M TEAPFOS-ACN as the electrolyte solution. This was made in order to characterize
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21 the oxidation and reduction behavior of the film. The *in situ* FTIR-ATR spectra were recorded
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23 during a slow voltammetric scan (2 mV s^{-1}) between -0.8 and 0.52 V with 0.12 V potential
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25 intervals. Twenty-five interferograms were recorded for each spectrum with 4 cm^{-1} spectral
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27 resolution. The measured spectra were compared to a reference spectrum recorded at -0.8 V
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29 which was recorded after pretreatment for 30 s at this potential. The spectra shown later in
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31 Figure 2 therefore describe the spectral differences from the reference state.
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39 **Potentiometric measurements.** Potentiometric measurements carried out in this work
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41 including the determination of the selectivity coefficients, O_2 , CO_2 and light sensitivity of the
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43 K^+ -SCISEs were made using a 16-channel high input impedance voltmeter (Lawson Labs, Inc.
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45 Malvern, PA). All other details are provided in the Supporting Information.
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50 51 **Results and discussion**

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53 **Characterization of the PPy-PFOS solid contact.** The CVs of three identical PPy-PFOS
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55 solid contacts measured in 0.05 M TEAPFOS-ACN solution are shown in Figure 1 revealing
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57 that the oxidation of the PPy film to its electrically conducting form occur at $E > \text{ca. } -0.6 \text{ V}$ in
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3 a reproducible manner. The low oxidation potential is typical for PPy prepared with a bulky
4 immobile anion such as dodecylsulphate⁶³ and makes the PPy-PFOS film electrically
5 conducting already at relatively low negative potentials. Potentiometric measurements of the
6 bare PPy-PFOS film in the presence of TEAPFOS showed a sub-Nernstian cationic slope of
7
8 conducting already at relatively low negative potentials. Potentiometric measurements of the
9 bare PPy-PFOS film in the presence of TEAPFOS showed a sub-Nernstian cationic slope of
10 25.6±3.8 mV/decade ($n=4$) at concentrations between 10^{-3} M to 10^{-2} M (data not shown)
11 suggesting that the film is dominantly exchanging cations (TEA^+) when it is cycled in the
12 TEAPFOS-ACN electrolyte solution (Figure 1). No potentiometric response was observed in
13 $10^{-3} - 10^{-1}$ M KCl as the electrolyte solution.
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42 **Figure 1.** CVs of three identically prepared PPy-PFOS solid contacts recorded in 0.05 M
43 TEAPFOS-ACN solution.
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47 The *in situ* FTIR-ATR measurements carried out on the PPy-PFOS films electropolymerized
48 on Pt sputtered ZnSe confirmed that the transition from the reduced form to the electrically
49 conducting oxidized form occurs between ca. -0.55 V to -0.2 V (Figure 2). In this potential
50 range, the infrared active vibrational (IRAV) bands of PPy, which are characteristic for the
51 conducting form of PPy-PFOS, grow in intensity with the main bands located at 852, 897,
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3 1053, 1167, 1344, 1460 and 1572 cm^{-1} . The wavenumbers are taken from the spectra
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5 measured at 0.16 V. The bands at 852 and 897 cm^{-1} are assigned to C-H out-of-plane bending
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7 and the band at 1053 and 1344 cm^{-1} to C-H in-plane bending.⁶⁴ The shift of the band at 1053
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9 cm^{-1} to higher energies upon oxidation may be explained by the higher energy required to
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11 bend the longer bonds in the quinoid form of PPy-PFOS. The band at 1167 cm^{-1} is assigned to
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13 pyrrole ring breathing vibrations which are symmetrical expansion and contraction
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15 movements without involving changes in bonding angles.⁶⁴ The bands at 1344, 1460 and
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17 1572 cm^{-1} are associated with C-N and C-C symmetric ring stretching vibrations, although the
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19 band at 1572 cm^{-1} predominantly arises from C=C stretching vibrations.^{64,65} On the other hand,
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21 the shifts of these bands towards lower energies may be explained by the lower energy
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23 required to stretch the longer bonds formed upon oxidation in the quinoid form of PPy. The
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25 charging-discharging reaction of ECP films is highly dependent on the nature of the doping
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27 ion resulting in some shifts of the IRAV bands of PPy-PFOS compared to PPy doped with
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29 other counter ions (LiClO_4 , NaClO_4 and dodecylsulphate).⁶⁶ The broad absorbance above
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31 1700 cm^{-1} that increases with the applied potential is characteristic for ECPs and assigned to
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33 the formation of charge carriers in the polymer matrix and the conversion of PPy-PFOS into
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35 the conducting state.⁶⁷
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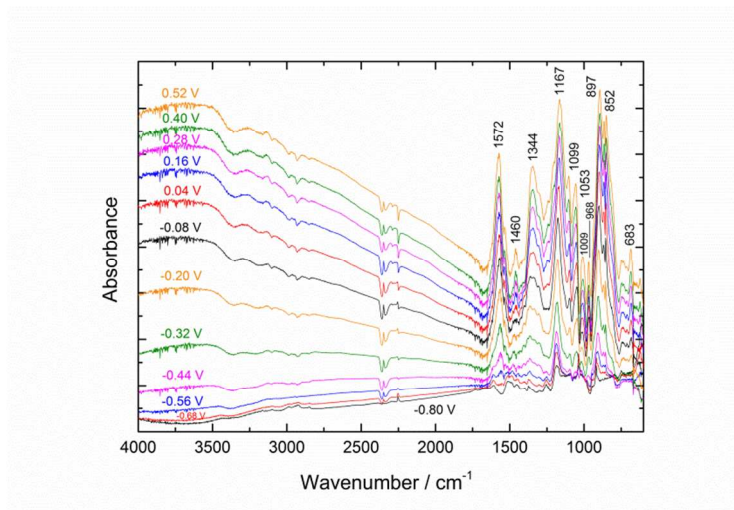


Figure 2. *In situ* FTIR-ATR spectra of the PPy-PFOS film measured in 0.05 M TEAPFOS-ACN in the potential range of -0.8 V to 0.52 V with 0.12 V potential intervals. The wavenumbers shown are taken from the spectra measured at 0.16 V.

Figure S-1 is a typical top view obtained by SEM of the PPy-PFOS film revealing that the film has a cauliflower-like and relatively compact morphology with some minor surface roughness. Unlike the SEM image shown in ref. 52 and 56, the mixed chemical and electrochemical polymerization method results in a more compact film rather than a rough and porous PPy film structure. This can be due to the difference in the electrode substrate used in this work (GC) and in ref. 56 (Au), but also to the rather low $\text{FeCl}_3 \cdot 6 \text{H}_2\text{O}$ concentration of 2×10^{-4} M. The PPy-PFOS film in Figure S-1 had a thickness of ca. $1.4 \mu\text{m}$ that was measured from the cross section of the film. The WCA of the PPy-PFOS films polarized for 10 min at -0.4 V and 0.2 V were $67 \pm 17^\circ$ and $97 \pm 5^\circ$ ($n=3$), respectively. This shows that the films are more hydrophobic in their conducting form, contrary to most other ECPs, and that the higher pre-polarization potential facilitates the incorporation of larger amounts of PFOS anions into the PPy matrix.

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3 **Pre-polarization of PPy solid contacts.** A major advantage of ECP-based SCs as compared
4 with those featuring solely capacitive stabilization is that the E^0 values of the respective
5 SCISEs can be adjusted by an applied external potential. However, this potential adjustment
6 is of practical use only if a stable state of the SC is reached by the applied potential to
7 guarantee long-term potential stability. Otherwise, the SCISEs will slowly drift to an
8 equilibrium state. We found that it is better to make the potential adjustment of the SCs before
9 the ISMs are applied to not involve mass transport through the ISM. To find out the
10 equilibrium potential, the bare PPy-PFOS solid contacts (without the ISM) were polarized in
11 0.05 M TEAPF₆-ACN at -0.4 V and 1.0 V, and then placed in direct contact with aqueous 0.1
12 M KCl solution at ambient oxygen conditions. Figure 3 shows relatively large potential drift
13 for the differently pre-polarized PPy films during the first 6-8 h. After 24 h the potential had
14 stabilized at ca. 0.18 V. To minimize the potential drift of the K⁺-SCISEs originating from the
15 buried solid-contact, the PPy solid-contact was therefore pre-polarized at 0.18 V for 10 min to
16 adjust the oxidation state of the ECP to a suitable level for the use of the SCISEs in the KCl
17 solutions. Given the low oxidation potential of PPy-PFOS, the pre-polarization potential of
18 0.18 V is high enough to convert the film to its oxidized conducting form (cp. with the FTIR-
19 ATR spectra in Figure 2).

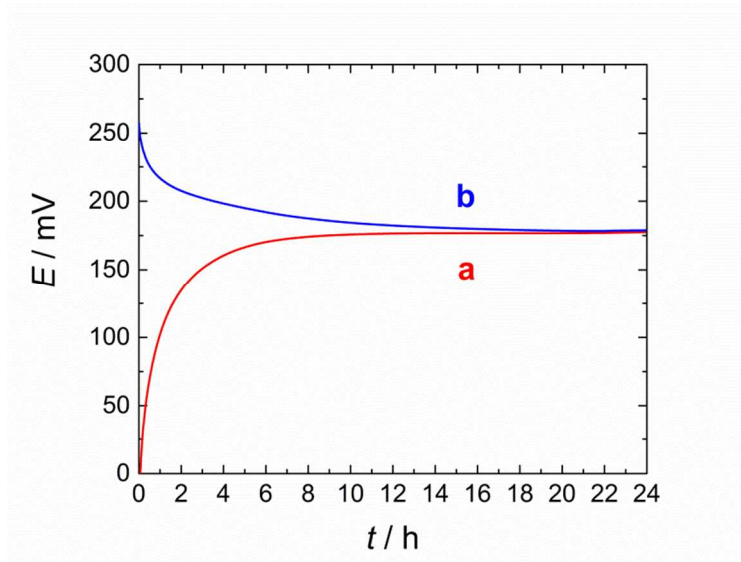


Figure 3. The potential stability of the PPy-PFOS films measured in 0.1 M KCl for 24 h after pre-polarization at (a) -0.4 V and (b) 1.0 V.

Water uptake of the PPy-PFOS solid contact. The water uptake of plasticized PVC-ISMs has been recently characterized by the FTIR-ATR spectroscopy^{29,30,68} and the oven based coulometric Karl Fischer titration technique.⁶⁸ It was shown that water diffuses readily through the PVC-ISMs and that the water content of the membrane is influenced by the chemical composition of the electrolyte solution contacting the ISM. It was found that the water content was highest when the ISM was in contact with deionized water while the water content of the ISM decreased in 0.1 M CaCl_2 solution.⁶⁸ In deionized water, the diffusion of water in the plasticized PVC-ISM was best described by a model consisting of two diffusion coefficients related to fast (ca. $1.4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) and slow ($1.2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$) water transport in the PVC membranes.³⁰ Therefore, before applying the ISM on top of the PPy-PFOS solid contact, we have studied the water barrier properties of the bare PPy-PFOS film pre-polarized at 0.18 V with the FTIR-ATR spectroscopy in the extreme situation when the SC is fully exposed to water without the protecting PVC-ISM top layer. This was done to predict how the

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3 SC will behave if it comes in contact with water. However, it should be remembered that as a
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5 buried layer beneath the ISM, the PPy-PFOS solid-contact is exposed to only very minor
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7 amounts of water (ca. 50-500 ppm), corresponding to the water concentration in plasticized
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9 PVC membrane.⁶⁸ The FTIR-ATR spectra measured during the water uptake of the PPy-
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11 PFOS solid contact is shown in Figure 4. After exposure of the PPy-PFOS film to water at $t=0$
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13 min, the gradually increasing OH stretching bands of water at ca. $3000-3700\text{ cm}^{-1}$ ^{29-31,57,69}
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15 reveal that the water uptake of the SC is very slow. The penetration depth of the IR beam is ca.
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17 $0.5-0.6\text{ }\mu\text{m}$ in this wavenumber region. Due to the absence of water bands in the very
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19 beginning of the FTIR measurement ($t=1\text{ min}$), it is assumed that the evanescent field of the
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21 IR beam penetrates only the PPy film (included in the background spectrum) in the
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23 wavenumber region of $3000-3700\text{ cm}^{-1}$. On the other hand, at 1640 cm^{-1} where the first
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25 overtone of the O-H stretching vibrations of water has its absorbance maximum, the
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27 penetration depth of the evanescent field is ca. twice higher (ca. $1.1-1.3\text{ }\mu\text{m}$) and due to the
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29 non-uniform film thickness of ca. $265-680\text{ nm}$ (the PPy film is thicker at the film edges), the
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31 evanescent field penetrates both the PPy-PFOS film and water already from the very
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33 beginning of the water uptake measurements. A strong water band at 1640 cm^{-1} is therefore
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35 observed in the first water uptake spectrum measured at $t=1\text{ min}$ (not shown). Mathematical
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37 simulations^{29,31} based on the integrated absorbance of the OH-stretching bands at $2720-4060$
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39 cm^{-1} (see Supporting Information) showed that the water diffusion in the PPy-PFOS film
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41 could be described with a model consisting of two diffusion coefficients: $D_1=9\times 10^{-13}\text{ cm}^2\text{ s}^{-1}$
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43 and $D_2=2\times 10^{-14}\text{ cm}^2\text{ s}^{-1}$ (Figure S-2). The diffusion coefficients reveal that the water diffuses
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45 slowly through the PPy-PFOS film and that it acts as an efficient water barrier. However, the
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modelled water diffusion coefficients should be considered only as approximate as the modelling was carried out with the mean film thickness of 472 nm.

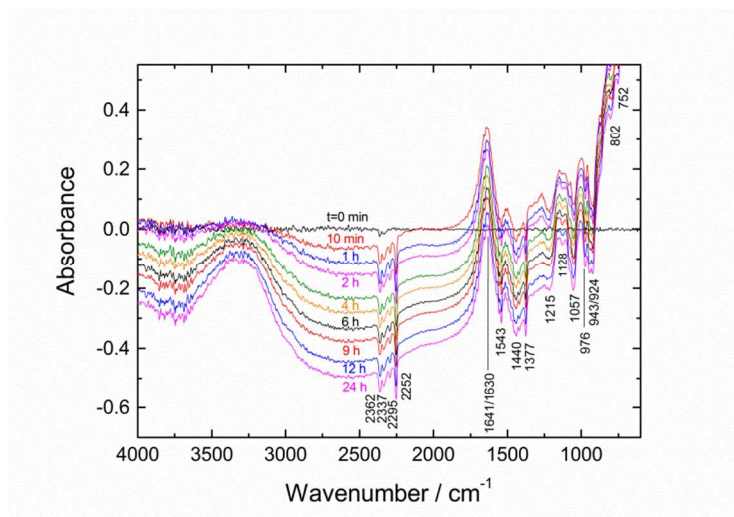


Figure 4. The FTIR-ATR spectra measured during the water uptake of the neat PPy-PFOS solid contact in deionized water during 24 h.

Simultaneously with the increasing water bands in the FTIR-ATR spectra in Figure 4, the spectral drift to negative absorbance values show that the PPy-PFOS film is slightly reduced during the water uptake measurements. The spectra in Figure 4 were measured with a signal amplification of 64 (included in the figure) and the real spectral changes are therefore smaller than what is shown in Figure 4. The decrease of the oxidation state of PPy is especially clearly seen at wavenumbers $> 1700 \text{ cm}^{-1}$, which is characteristic for the broad electronic absorbance band of the ECPs.⁶⁷ Also, several downward pointing negative IR bands related to PPy, PFOS⁻ and ACN overlap with the increasing water bands in the IRAV region at wavenumbers $< 1500 \text{ cm}^{-1}$. The band assignments are given in Table S-1 in the Supporting Information. It should be noted that the bands of the conducting form of PPy, the PFOS⁻ anion and traces of ACN are all included in the background spectrum of the PPy-PFOS film and therefore they decrease in intensity as the film is reduced (*i.e.* its oxidation state is lowered).

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3 In Figure 4, the negative vibrational band at 1128 cm^{-1} ascribed to asymmetric SO_3 stretching
4 vibration in PFOS^- ,⁷⁰ which increases in intensity with time, indicates that some of the PFOS^-
5 leaves the film during the water uptake measurements. The concentration gradient of PFOS^-
6 between the PPy film and deionized water is expected to be the main driving force for some
7 of the PFOS^- anions to diffuse from the PPy matrix to the solution phase.
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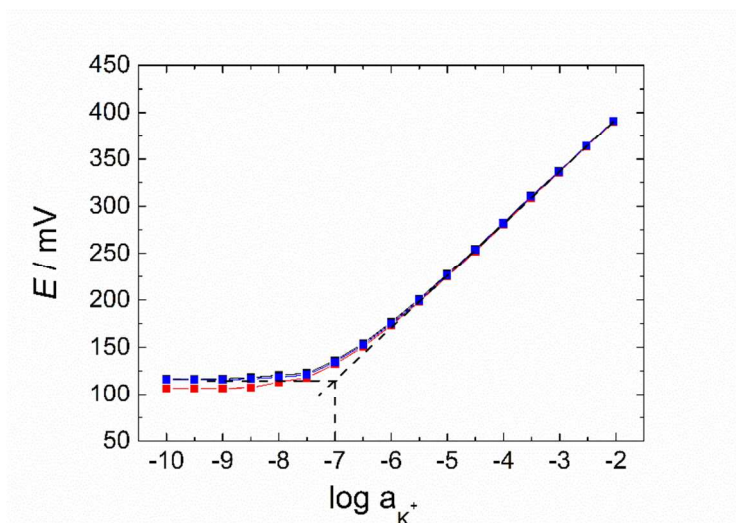
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17 When the PPy-PFOS is applied as the SC beneath the PVC-ISM, the oxidation state changes
18 are expected to occur only to a very minor extent compared to the changes in Figure 4 and the
19 PPy film should therefore retain its hydrophobicity under the ISM. However, it can be
20 speculated that slow changes in the oxidation state can possibly occur over longer time
21 periods due to the (low) water solubility of PFOS^- if the SC comes into contact with water
22 diffusing through the ISM.
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34 **Initial potential stability and calibration of the K^+ -SCISEs.** The pre-polarization of the
35 SCs to a stable form may be also beneficial in terms of achieving much shorter conditioning
36 times.⁷¹ It was found that the K^+ -SCISEs reached a stable potential after 1 h from their very
37 first contact with unstirred aqueous 0.1 M KCl solution (not shown). After stabilization of the
38 potential during the first hour, the SCISEs showed a relatively low potential drift of $-71\ \mu\text{V h}^{-1}$
39 for the next 15 h. The potential traces and calibration graphs of the K^+ -SCISEs in 10^{-10} - 10^{-3}
40 M KCl solutions are shown in Figure S-3 and Figure 5, respectively. The electrodes gave a
41 linear potentiometric response up to 0.1 M KCl (not shown) and showed a close to Nernstian
42 slope of $57.0\pm 0.1\text{ mV/decade}$ ($r^2=0.999$). The LOD was $(8.8\pm 2.1)\times 10^{-8}\text{ M}$ if the electrodes
43 were conditioned at low KCl concentrations (10^{-9} M) prior to the calibration and limiting the
44 calibration up to 1 mM KCl (Figure 5). In Figure S-3, the potentials were measured with
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3 intervals of one second during 300 s at each Ca^{2+} concentration and the potential values
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5 shown in Figure 5 were taken in the very end of this 5 min period. The selectivity coefficients
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7 ($\log K_{\text{K}^+, \text{J}}^{\text{pot}}$) of the K^+ -SCISEs for most relevant interfering ions in biological samples was
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9 found to be between -4.5 to -5.6 (except of $\text{J}=\text{NH}_4^+$) as shown in Table S-2.⁷² The optimized
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11 K^+ -SCISEs showed in the best case a very good E^0 reproducibility of only 501.0 ± 0.7 mV
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13 ($n=4$) with a SD that is equal to that obtained for the redox buffer based SCISEs (± 0.7 mV)⁵⁵
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15 and which surpasses the SDs of the state of the art ECP based SCISEs (usually ca. ± 20 mV).⁵¹
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17 The improved E^0 reproducibility of the K^+ -SCISEs is ascribed to the combination of the pre-
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19 polarization and hydrophobicity of the PPy-PFOS solid contact counteracting the detrimental
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21 aqueous layer/pool formation beneath the ISM. This reproducibility was confirmed in a
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23 subsequent batch ($n=3$). However, we started to see larger deviation in E^0 within a batch and
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25 batch-to-batch when we increased the number of electrodes in an interlaboratory study. Two
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27 factors were identified to lead to these larger deviations: (i) there were GC substrate
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29 electrodes that even after multiple re-making of the SCISEs showed consistently E^0 values far
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31 from the mean value suggesting that the quality of the substrate electrodes may influence the
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33 E^0 ; ⁷³ (ii) a larger deviation from E^0 was also obtained for the K^+ -SCISEs prepared at the two
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35 co-operating laboratories (authoring this paper) by using the same protocols, but different
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37 instrumentation and batches of chemicals for the SC and ISM preparation. For the best E^0
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39 reproducibility we removed these electrodes and the ± 0.7 mV represents conditions where the
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41 above mentioned factors do not influence the SD of the E^0 . This suggests that the current
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43 practice of E^0 reproducibility determination generally based on a small batch of electrodes
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45 may need to be extended to larger batches and that the quality of the substrate electrodes may
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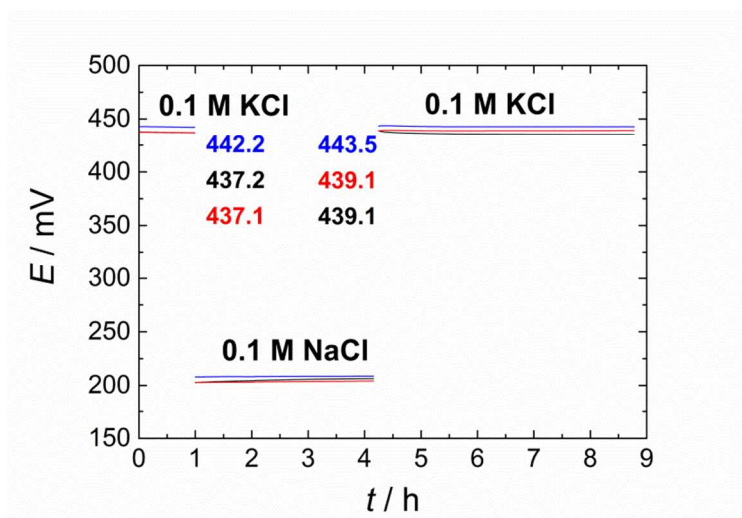
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3 need to be carefully considered. The latter requirement would be probably best addressed by
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5 using microfabricated substrate electrodes and clean-room conditions.
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10 After keeping the K^+ -SCISEs in 10^{-4} M KCl for 46 days, the electrodes showed a Nernstian
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12 slope of 58.1 ± 0.2 mV/decade ($r^2=0.999$), but almost one decade higher LOD of $(6.4 \pm 1.0) \times 10^{-}$
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14 7 M than for the freshly prepared SCISEs (not shown). However, no special pre-treatment
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16 protocols at low KCl concentrations were applied to these electrodes before starting the
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18 calibration that can partially explain the higher detection limit. Regardless of the higher LOD,
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20 the K^+ -SCISEs showed a very good E^0 reproducibility of 577.1 ± 3.1 mV ($n=3$) still after 46
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22 days, which equals to a relatively low E^0 drift of $69 \mu\text{V h}^{-1}$ during this time period. This
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24 additionally proves the robustness of the K^+ -SCISEs. In comparison, the SD of E^0 for the
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26 redox buffer based SCISEs ($n=5$) had increased from 0.7 mV ($t=1$ h) to 16.3 mV already
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28 during the first 24 h of use.⁵⁵ During this time the SCISEs showed a potential drift of ca. 0.6
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30 mV h^{-1} .
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3 **Figure 5.** The calibration graphs of PPy-PFOS based K^+ -SCISEs ($n=3$). The dashed lines
4 illustrate the determination of the LOD.
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9 **Potentiometric aqueous layer test.** Due to the water uptake of the plasticized PVC-ISMs, it
10 is possible that a water layer forms beneath the ISM in the SCISE structure. We investigated
11 this possibility with the potentiometric aqueous layer test (Figure 6).³² The lack of potential
12 drifts upon changing between solutions with high concentration of primary (K^+) and
13 interfering (Na^+) ions, as shown in Figure 6, revealed no indications of an aqueous layer
14 formation. This indicates that the PPy-PFOS solid contact acts as an efficient water barrier,
15 which is very unusual since it is difficult to avoid aqueous layer formation for SCISEs
16 prepared with PVC-ISMs which have a relatively high water uptake.³⁰ This has been achieved
17 only in a few cases, e.g. by using hydrophobic polyazulene⁷⁴ and PPy doped with
18 hexacyanoferrate (II)/(III)⁵¹ as the SCs in K^+ -SCISEs. The absence of the aqueous layer
19 formation has been also reported for poly(3-octylthiophene) (POT) based Ca^{2+} -SCISEs by
20 using chemically prepared and almost electrically non-conducting POT as the SC.⁷⁵
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55 **Figure 6.** Potentiometric aqueous layer test of PPy-PFOS based K^+ -SCISEs ($n=3$).
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3 The electrode potentials in Figure 6 are practically the same before and after exposure to 0.1
4 M NaCl solution for 4 h showing the good potential stability of the SCISEs. In Figure 6, the
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6 M NaCl solution for 4 h showing the good potential stability of the SCISEs. In Figure 6, the
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8 K^+ -SCISE potentials in 0.1 M KCl are ca. 57 mV higher than for 10^{-2} M KCl in Figure 5
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10 (calibration graph) showing that the electrodes had a Nernstian response between 10^{-2} M and
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12 0.1 M KCl. No sulphur could be detected at 2.3 keV⁷⁶ neither on the top (solution side) nor
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14 the bottom side (facing the SC) of the PVC-ISM in the energy dispersive X-ray spectra of
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16 freshly prepared K^+ -SCISEs that had not been in contact with water. This indicates that the
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18 bulky PFOS⁻ anions stay in the PPy solid contact making it hydrophobic and do not diffuse
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20 into the PVC-ISM during the electrode preparation. The absence of the aqueous layer
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22 formation in Figure 6 reveals also that the oxidation state of the PPy-PFOS solid contact is
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24 unaffected beneath the ISM. It therefore functions as an efficient water barrier in accordance
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26 with the low water diffusion coefficients obtained by the mathematical modelling.
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34 **Carbon dioxide, oxygen and light sensitivity.** The PPy-PFOS based K^+ -SCISEs showed no
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36 light sensitivity and a very minor drift of only -0.7 mV h^{-1} when the 0.1 M KCl solution that
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38 was first purged with N_2 was saturated with CO_2 . A similar small drift of ca. 1.8 mV h^{-1} was
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40 observed when switching from oxygen-free 0.1 M KCl solution to air saturated (Figures S-4 -
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42 S-6). The O_2 and CO_2 changes are more drastic than in most practical situations and are
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44 indicative of the worst case scenario.
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50 CONCLUSIONS

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52 We have used for the first time PPy doped with the hydrophobic PFOS⁻ anions as the ion-to-
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54 electron transducer in K^+ -SCISEs. The PPy transducers that are usually hydrophilic in their
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56 conducting form can thus be made hydrophobic with PFOS⁻ (WCA: $97 \pm 5^\circ$). The K^+ -SCISEs
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3 have in the best case a very good E^0 reproducibility of only ± 0.7 mV, which is attributed to
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5 the combination of the pre-polarization of the PPy-PFOS solid contact and its excellent water
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7 barrier properties due to its high hydrophobicity. Mathematical modelling revealed that the
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9 water uptake of the PPy-PFOS film measured with the FTIR-ATR spectroscopy was best
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11 described with a model consisting of two diffusion coefficients, $D_1=9\times 10^{-13}$ cm² s⁻¹ and
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13 $D_2=2\times 10^{-14}$ cm² s⁻¹ showing that the diffusion of water through the PPy-PFOS solid contact is
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15 very slow. PFOS⁻ was used in this work as a model compound, but because of its
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17 environmental risks, it is desirable to replace it with a more environmentally friendly
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19 hydrophobic compound.
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28
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30
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32
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41 contact angle measurements.
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49 **ASSOCIATED CONTENT**

50 **Supporting Information**

51
52 Experimental descriptions of the electropolymerization of pyrrole on the ZnSe reflection
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54 element, potentiometric measurements including the determination of the selectivity
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3 coefficients, O₂, CO₂ and light sensitivity. Mathematical modeling of the water diffusion
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5 coefficients in the PPy-PFOS film and the assignments of its FTIR bands. SEM image of the
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7 PPy-PFOS film, potentiometric selectivity coefficients and potential traces of the K⁺-SCISEs
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9 in 10⁻¹⁰-10⁻² M KCl solutions.
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