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Ferrocene Bound Poly(vinyl chloride) as Ion to Electron Transducer in Electrochemical Ion Sensors

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We report here on the synthesis of poly(vinyl chloride) (PVC) covalently modified with ferrocene groups (FcPVC) and the electrochemical behavior of the resulting polymeric membranes in view of designing all solid state voltammetric ion sensors. The Huisgen cycloaddition ("click chemistry") was found to be a simple and efficient method for ferrocene attachment. A degree of PVC modification with ferrocene groups between 1.9 and 6.1 mol % was achieved. The chemical modification of the PVC backbone does not significantly affect the ion-selective properties (selectivity, mobility, and solvent casting ability) of potentiometric sensing membranes applying this polymer. Importantly, the presence of such ferrocene groups may eliminate the need for an additional redox-active layer between the membrane and the inner electric contact in all solid state sensor designs. Electrochemical doping of this system was studied in a symmetrical sandwich configuration: glassy carbon electrode |FcPVC| glassy carbon electrode. Prior electrochemical doping from aqueous solution, resulting in a partial oxidation of the ferrocene groups, was confirmed to be necessary for the sandwich configuration to pass current effectively. The results suggest that only ~2.3 mol % of the ferrocene groups are electrochemically accessible, likely due to surface confined electrochemical behavior in the polymer. Indeed, cyclic voltammetry of aqueous hexacyanoferrate (III) remains featureless at cathodic potentials (down to -0.5 V). This indicates that the modified membrane is not responsive to redox-active species in the sample solution, making it possible to apply this polymer as a traditional, single membrane. Yet, the redox capacity of the electrode modified with this type of membrane was more than 520 μC considering a 20 mm² active electrode area, which appears to be sufficient for numerous practical ion voltammetric applications. The electrode was observed to operate reproducibly, with 1% standard deviation, when applying pulsed amperometric techniques.

Poly(vinyl chloride) is a polymeric matrix commonly used for electrochemical electrode preparation, and is popular in classical

aqueous inner contact¹ and solid state electrode (SSE) configurations^{2–10} because of its attractive mechanical properties and compatibility with electro-active components. With SSEs, an effective ion-to-electron transduction is necessary,^{2,3} which is usually applied as a separate layer between the ion-selective membrane (ISM) and the inner metallic contact^{4–8} or as an additive to the membrane.⁹ The most popular redox-active materials used for this purpose are conductive polymers.^{4–6,9} Many types of such polymers have been successfully applied in potentiometric electrodes, e.g., poly(pyrrole) (PPy),^{4,5,11} poly(octyl thiophene) (POT),^{9,10,12} poly(3,4-ethylenedioxythiophene) (PEDOT),^{6,13,14} and poly(aniline) (PANI),⁹ and the suppression of a water layer between the conducting polymer and underlying electrode was found to be a key characteristic to guarantee stable potentiometric behavior.^{15–17} In recent years, ion-selective electrodes interrogated by voltammetric techniques have increased in importance.¹⁸ This class of sensors borrows materials and techniques from the fields of ion-selective electrodes and the electrochemistry at the interface

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of two immiscible electrolyte solutions (ITIES) and has allowed researchers to design reversibly operating polyion sensors,^{19–21} flash chronopotentiometric electrodes for rapid determination of kinetically labile components,²² ion channel mimetic systems,²³ thin layer coulometric sensors,²⁴ thin layer electrodes for stripping voltammetry,²⁵ as well as controlled current coulometric sensors.²⁶

The requirements for the realization of all solid state voltammetric ion sensors are more difficult to satisfy than the potentiometric sensors mentioned above, since the required redox capacity must be sufficiently high to sustain the ion transfer current. Shvarev showed that PEDOT is a promising conducting polymer underlayer for this purpose,²⁷ Amemiya^{25,28} and our group²⁹ studied conducting polymers for thin layer voltammetric applications. With these materials, the redox properties are typically conducive to anion extraction from the sample solution. To allow for cation extraction, the polymer may sometimes be doped to obtain its stable oxidized form.²⁹

An alternative strategy was suggested by Samec et al.³⁰ by the incorporation of lipophilic ferrocene derivatives. This appears to be an attractive alternative to conducting polymer based systems, owing to the well-defined reversible redox couple and a potentially high redox capacity of the resulting membranes. Freely dissolving such redox active species may, however, result in eventual leaching from the membrane (especially in its oxidized, positively charged form) and in interferences from redox active species in the sample.

To address these limitations and to introduce an alternative material, the chemical attachment of ferrocene groups to polymer chains is explored here. From a chemical point of view, poly(vinyl chloride) is easily modifiable due to the susceptibility for nucleophilic substitution of the chlorine atoms.^{31,32} The most commonly used method for introducing new functional groups into the PVC chain is the reaction with sodium azide.^{33,34} This modification was used for example in the cross-linking of the polymer.³⁵ Recently, the Huisgen cycloaddition, known also as “click chemistry”, has become a very popular method of transforming azide groups.³⁶ This type of reaction is attractive because of its high selectivity, mild reaction conditions, very high yields, and lack of byproducts. It was successfully applied for modification of a wide range of

different polymers,³⁷ but it has not yet become popular for the modification of PVC. Considering that the modified polymer is intended to be applied for electrochemical electrode preparation, any redox activity is expected to be related to the ferrocene groups only. The redox active properties of a triazol linker obtained by applying the Huisgen cycloaddition has been studied by Kirrs and co-workers,³⁸ revealing that it is indeed electrochemically inert. In this paper we present studies on properties of membranes containing poly(vinyl chloride) modified with ferrocene groups via the click-chemistry reaction.

EXPERIMENTAL SECTION

General Methods and Materials. High molecular weight poly(vinyl chloride) (PVC), sodium azide, ethynylferrocene, L-ascorbic acid, copper sulfate pentahydrate, tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH 500), bis(2-ethylhexyl) sebacate (DOS), potassium hexacyanoferrate (III), potassium chloride, sodium perchlorate, sodium nitrate, sodium thiocyanate, anhydrous tetrahydrofuran (THF), and dimethylformamide (DMF) were purchased from Sigma Aldrich and used without further purification. Aqueous solutions were prepared by dissolving the appropriate salts in Milli-Q-purified distilled water.

IR spectra were taken using a Perkin-Elmer Spectrum 100 FT-IR spectrometer with attenuated total reflectance (ATR) sampling accessory and ATR corrected. UV–vis spectra were recorded in the 900–350 nm wavelength range on a GBC UV–vis 916 spectrophotometer using 1 cm thick quartz cuvettes. The UV–vis calibration curve was obtained for three samples containing 2, 6, and 12 $\mu\text{mol/mL}$ of ferrocene dissolved in a matrix containing 33 mg of PVC per mL of THF. The first order derivative of the spectrum was used to determine the content of ferrocene attached to the PVC. Glassy carbon rods of 5 mm diameter were purchased from SPI Supplies/Structure Probe, Inc. (West Chester, PA) and assembled into an epoxy resin body (EpoFix Kit, Struers Australia, Milton QLD, Australia).

Synthesis. The substitution reaction of PVC with NaN_3 was carried out using 1 g (16 mmol based on monomeric unit) of PVC and 1.04 g (16 mmol) of NaN_3 in 42 mL of DMF–water mixture (5:1 volume ratio) and heated at 50 °C under nitrogen for various times from 24 to 168 h. When the desired degree of modification was achieved, the reaction mixture was cooled to room temperature, the product was filtered, washed with distilled water and methanol, and subsequently dried under reduced pressure. In the click-chemistry reaction between azide-modified PVC and ethynylferrocene, 300 mg of N_3PVC , 60 mg (0.29 mmol) of ethynylferrocene, 140 mg (0.56 mmol) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and 500 mg (2.84 mmol) of ascorbic acid were added to 28 mL of a THF–water mixture (6:1 volume ratio). After 4 h of reaction time, the product was precipitated with water. Ferrocene modified PVC was filtered, washed thoroughly with methanol, and then dissolved in 20 mL of THF. The THF solution was then filtered again to remove insoluble impurities, and the product was precipitated with methanol, filtered, and dried under reduced pressure.

Composition of Membrane Cocktails. Membrane cocktail was prepared by dissolving 7.5 mg of FcPVC, 37.5 mg of DOS,

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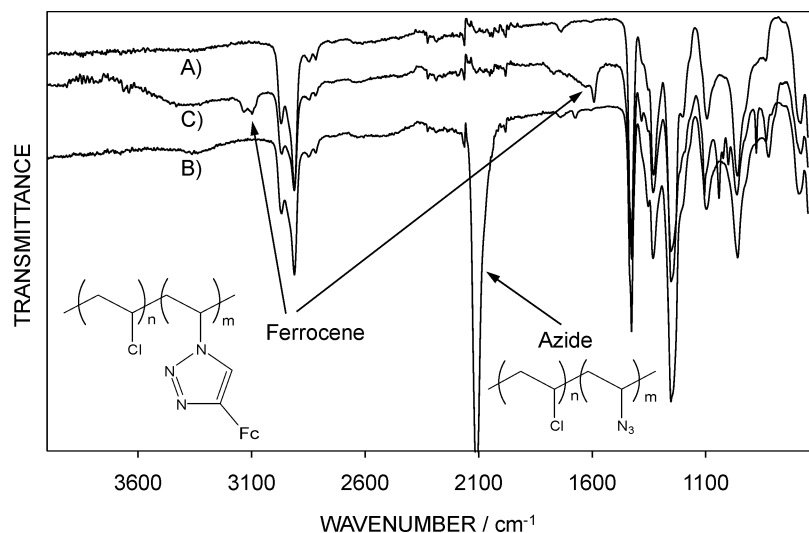


Figure 1. Infrared spectra of (A) unmodified PVC, (B) azide-modified PVC, and (C) ferrocene-modified PVC. Insets: structures of azide modified PVC and FcPVC.

and 5 mg of ETH 500 in 1 mL of THF. DOS is a plasticizer commonly used as a solvent in PVC-based (liquid) membranes. The lipophilic electrolyte ETH 500 is added to provide counterions for the extracted analyte in the membrane and is also used to keep the electrical resistance of the membrane low. Electrodes were prepared by drop casting 40 μ L of cocktail and letting the THF evaporate overnight under ambient conditions.

Electrochemical Experiments. All cyclic voltammetry experiments were performed at a 50 mV s⁻¹ scan rate. Normal pulse voltammograms were performed in a -0.6 to +0.8 V potential range using 10 mM solutions of NaCl, NaSCN, NaNO₃, and NaClO₄. Potential pulses (1 s) with a 20 mV potential increase were followed by a 5 s regeneration pulse (baseline potential) at open circuit potential (as measured before each voltammetric experiment). Membrane doping was performed with a single pulse of 10 min duration in a potential range of 400–800 mV in 10 mM NaClO₄. A time of 10 min was chosen experimentally as the shortest time allowing the observed current to sufficiently decay. In the sandwiched electrode experiment, a three pulse procedure was applied. The first 30 s pulse at 0 mV was to confirm the steady state of the system before a 300 s long pulse at 200 mV was applied to induce electrochemical processes, while the last, carried out for 300 s at 0 mV, was to allow the system to return to its original state.

Cyclic voltammetry in the presence of hexacyanoferrate(III) ion was performed in 1 mM K₃Fe(CN)₆ solution with 0.1 M KCl as a background, and the potential was scanned between a 0.8 and -0.5 V potential range starting from 0.4 V and going to negative potentials first. The stability of the signal generated by the FcPVC modified electrode was examined by application of a 1 s pulse at 0.5 V and followed by 20 s regeneration at the applied open circuit potential, using a three electrode configuration and 10 mM sodium perchlorate. The procedure was repeated 40 times. The redox capacity of the FcPVC was tested in the same solution by applying a 0.8 V potential for 30, 60, 120, 300, and 600 s, each time followed by a discharge pulse at 0 V for 200 s.

Table 1. Reaction Time of Azidation and Resulting Degree of Ferrocene Modification of PVC, Estimated by Spectrophotometry

reaction time [h]	degree of modification [mol %]
24	1.9
60	3.2
120	5.3
168	6.1

RESULTS AND DISCUSSION

In an initial step, PVC was modified with azide groups using NaN₃ according to Sacristan et al.³³ The efficiency of the reaction was confirmed by comparing the IR spectrum for commercial, not modified PVC, and the same polymer after modification with azide groups. As shown in Figure 1A,B, the distinctive azide band at 2100 cm⁻¹, not visible for unmodified PVC, gives a well developed peak after reaction, confirming the effective partial modification of the polymeric backbone with azide groups.

Further modification of azide-modified PVC with ferrocene groups required the use of a large excess of catalyst (200 mol % relative to the ethynylferrocene) to allow a high yield of reaction. As seen in Figure 1C, the IR spectrum for the reaction product did not reveal any signal from azide groups, indicating full conversion of the substrate. Since the ferrocene groups absorb strongly at 440 nm, the content of the ferrocene groups in the obtained FcPVC could be conveniently estimated from a calibration curve prepared for mixtures of nonmodified PVC with various ethynylferrocene contents dissolved in THF. Since the baselines for a THF solution of the ferrocene-modified PVC were significantly different, the ferrocene content was calculated based on spectral derivatives. On the basis of the spectrophotometric results and considering complete conversion of azide to ferrocene in the polymer backbone (as indicated by FT-IR) it may be concluded that the content of the ferrocene groups in PVC can be easily controlled by adjusting the time of azidation reaction. As shown in Table 1 for the polymer that has been modified with azide

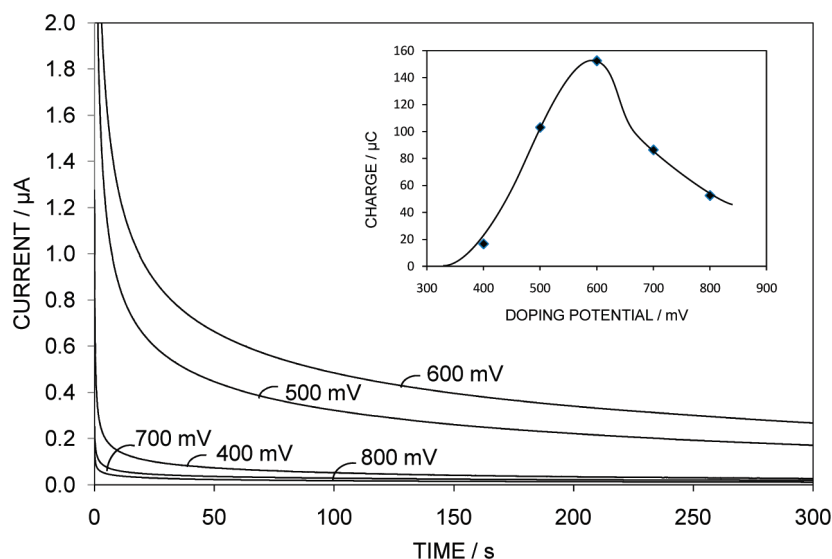


Figure 2. Chronoamperograms obtained for a pair of sandwiched electrodes modified with a FcPVC-DOS membrane containing 10 wt % of ETH 500, anodically doped with perchlorate from a 10 mM NaClO₄ solution at the indicated potentials. Inset: charge calculated from the chronoamperograms as a function of the doping potential.

groups in the first step reaction for only 24 h, the content of ferrocene groups attached during the second reaction step was 1.9 mol %. The degree of modification significantly increased to 3.2 mol % when the reaction time for the first step was increased to 60 h. After 120 h of the azidation, the reaction rate started to slow down while after 168 h the efficiency reached 6.1 mol % and its further increase was negligible.

Unfortunately, with higher conversion rate the solubility of the modified PVC in THF drops significantly. For example, the highest concentration that could be obtained for a membrane cocktail containing FcPVC with 3.2 mol % of ferrocene groups is 50 mg/mL of THF (which is half of the typical cocktail concentration when using unmodified PVC), while only 17 mg of the cocktail containing polymer with 6 mol % of ferrocene groups could be dissolved in the same volume. This property is most likely related to the presence of aromatic linker between the ferrocene group and polymer backbone, which may result in a loose cross-linking due to π -stacking. Therefore, for practical reasons FcPVC containing 3.2 mol % of ferrocene (461 mmol/kg) was chosen for further studies as a compromise between electrochemical activity and solubility.

In initial studies, the redox properties of FcPVC in the ion-selective membrane were studied independently of an aqueous electrolyte. The redox process at the inner side of the membrane is otherwise difficult to distinguish from the outer ion transfer process, which may be rate limiting owing to the low mobility of ion-selective membrane materials.^{39,40} Removal of the aqueous electrolyte was achieved here in a fully symmetrical cell, sandwiching the ion-selective ferrocene functionalized membrane between two glassy carbon (GC) electrodes. Note that a fully reduced ferrocene based membrane is not expected to pass current effectively, since any oxidation at one electrode must be accompanied by a concurrent reduction at the second electrode. Ideally, therefore, the membrane must be composed of a reduced

and oxidized form in a one to one molar ratio for the following reaction to occur efficiently:



This was confirmed here by an electrochemical doping step from sodium perchlorate solution prior to assembling the sandwich configuration. Two identical glassy carbon electrodes modified with a FcPVC/DOS/ETH 500 membrane were placed in 10 mM NaClO₄ solution and held at 400 mV for 600 s to partially oxidize ferrocene groups by incorporation of perchlorate ions into the membrane. Immediately after the doping process, the electrodes were sandwiched together. A potential of 200 mV was applied between the two electrodes for 300 s and the current recorded (see Figure 2). The observed current very soon decayed to near zero values, indicating a low ferrocenium concentration in the membrane. The total number of coulombs calculated from the integral of the chronoamperogram was 16.45 μC . After electrode separation, they were again immersed into the doping solution and held at 500 mV for the same time period. The sandwich procedure was repeated and higher currents were observed, resulting in a charge of 102.88 μC . This experimental sequence was repeated for increasing doping potentials. A plot of calculated charge as a function of doping potential is presented in the inset of Figure 2. Doping potentials higher than 600 mV gave a decreasing charge, consistent with ferrocene as a limiting reagent in reaction 1 above. Note that more positive potentials may also result in the oxidation of the tetraphenylborate anion,²⁸ a component of the lipophilic electrolyte, and hence may explain the observed distortion of the expected bell-shaped curve (number of coulombs vs doping potential) at larger potentials.

From the maximum charge found for the optimally doped electrodes it can be calculated that the amount of ferrocenium/ferrocene groups participating in the process was 3.16 nmol per 20 mm² of electrode area, or about 10 mmol kg⁻¹ (of which

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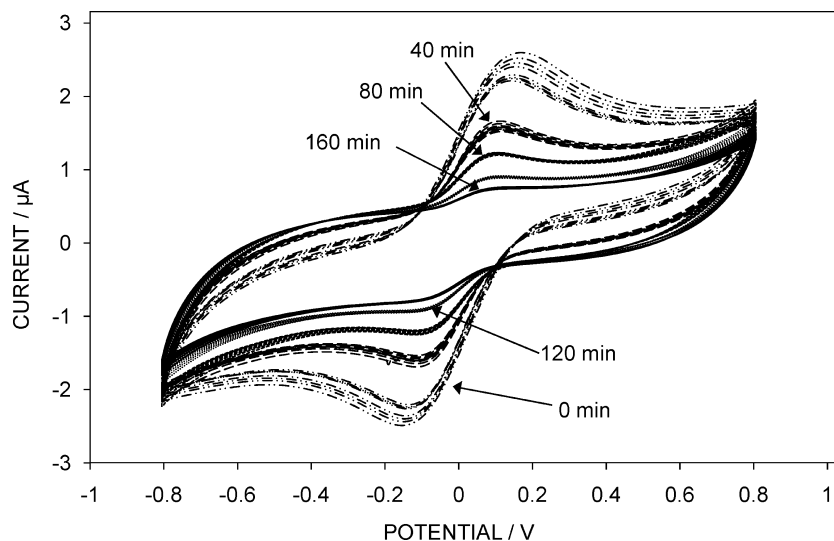


Figure 3. Cyclic voltammograms obtained for a pair of sandwiched electrodes modified with FcPVC membrane containing 461 mmol/kg of ferrocene groups and 10 wt % of ETH 500 anodically doped from 10 mM NaClO₄ solution at 600 mV carried out for the indicated times after the doping.

half can be oxidized and half reduced). This is just about 2.3 mol % of what was calculated based on the spectrophotometric calibration curve. Considering that the mobility of ferrocene/ferrocenium groups attached to a long chain of the polymer is limited, only the molecules being at a close distance from the glassy carbon electrode may participate in the electrochemical processes within the experimental time frame. This, however, may be an advantage considering the method presented here, since it suggests that the material is insensitive to redox active species in the contacting aqueous solution (see below).

When cyclic voltammetry was performed on a freshly doped sandwiched system, a redox couple was observed, with oxidation and reduction peaks comparable to the theoretical shape obtained for ferrocene dissolved in acetonitrile on a gold electrode.⁴¹ The peak heights for the oxidation and reduction processes were almost identical indicating that the system is fully reversible. The peaks were separated by 320 mV which is more than in the case of ferrocene dissolved in acetonitrile (56 mV). This is not unexpected, given the fact that ferrocene is attached to the PVC backbone (and not diffusion limited as in the theoretical case) and the second electrode is acting as both the counter and reference electrode. However, for successive scans important changes of the maximum and minimum current values were observed. A series of 10 scans was repeated 40, 80, 120, and 160 min after doping and showed that the maximum peak currents successively diminished with time (Figure 3). On the basis of our previous observations that within the time frame of the doping experiment (600 s) only about 2% of redox-active groups undergo oxidation, the decrease of observed currents may be explained by the gradual diffusion of oxidized ferrocene away from the electrode surface into the surrounding bulk membrane. Functionalities covalently attached to the PVC backbone are indeed not strictly immobile, as evidenced by earlier work demonstrating

equilibration of solvent cast plasticized PVC films with covalently attached chromophore functionalities throughout the bulk of the material.⁴²

Subsequent work focused on three electrode systems in order to characterize the solid state membrane in contact with aqueous electrolyte. The ion-selective properties of the new polymer were studied in 10 mM solutions with normal pulse voltammetry, which has been established as a robust and gentle method of ion-selective membrane characterization.⁴³ The results are presented in Figure 4. The potentials at which the ion transfer of ClO₄⁻, SCN⁻, NO₃⁻, and Cl⁻ ions occur at a current of 1 μA were found at about 420, 460, 580, and 700 mV, respectively. The order and the magnitude of the potential separation are consistent with the theoretical selectivity expected for lipophilicity-based extraction according to the Hofmeister series.⁴³ This confirms that the ferrocene modification has a negligible effect on the anion extraction properties of the polymer. When scanning the electrode to a negative potential range, a cation extraction wave should normally occur with aqueous inner contact systems.⁴⁴ The inset of Figure 4 suggests for the sodium chloride sample that the voltammogram is very quiet at cathodic potentials, suggesting no cationic response. As mentioned above, the ferrocene groups present in the polymeric phase are predominately in their reduced state, suppressing cathodic response. It is expected that doping the membrane with lipophilic cation-exchanger according to a procedure recently reported for poly(octyl thiophene) (POT)²⁹ will allow one to yield cation transfer voltammetric characteristics, but this was not pursued here.

Ferrocene groups are randomly distributed in the membrane phase and hence some of them are believed to be present on the membrane surface. Exposure of the conductive groups to the sample solution may cause undesired electrode sensitivity to redox-active solutes. Therefore, the studied electrodes were tested

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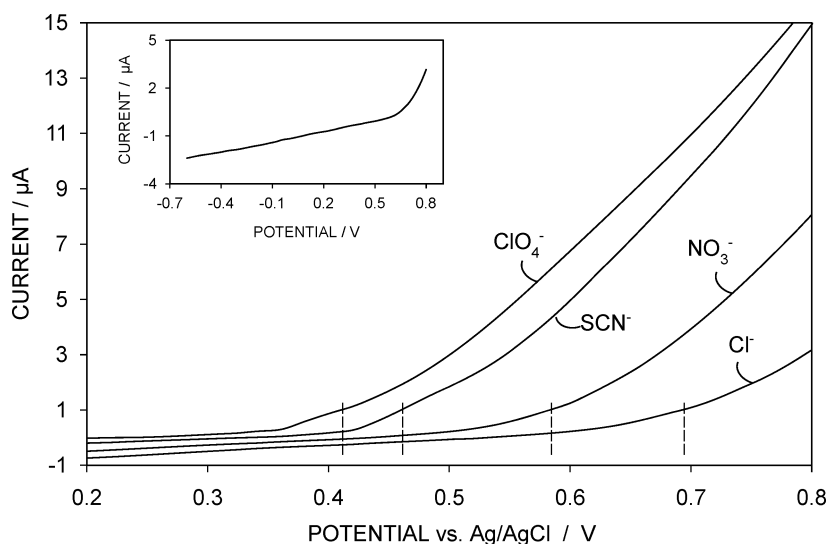


Figure 4. Normal pulse voltammograms for an electrode modified with FcPVC-DOS with 10 wt % of ETH 500 performed in 10 mM solutions of the indicated anions. Inset: Response behavior to sodium chloride at more negative potentials, demonstrating the suppression of cation transfer processes.

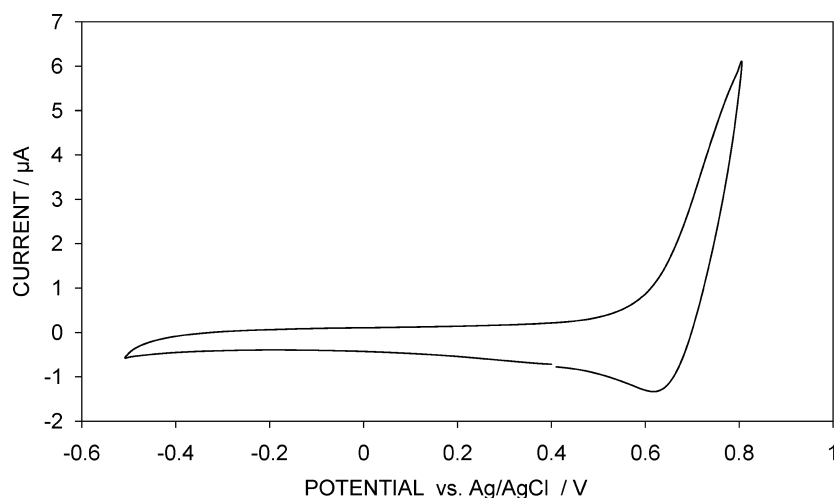


Figure 5. Cyclic voltammogram for an FcPVC modified electrode in 1 mM solution of $K_3Fe(CN)_6$ and 0.1 M KCl.

for redox sensitivity in the presence of potassium hexacyanoferrate(III), which is known to undergo extraction into the organic phase at positive potentials,⁴⁵ giving anodic currents, while the undesired reduction of the Fe(III) species mediated by FcPVC should result in cathodic currents at negative potentials. To evaluate this, electrodes were scanned from -0.5 to 0.8 V in aqueous hexacyanoferrate(III) solutions (Figure 5). The cyclic voltammograms revealed indeed an anodic anion extraction wave at positive potentials, together with its subsequent stripping on the return scan. On the other hand, the cyclic voltammogram in the 0.4 to -0.5 V potential range remained featureless, suggesting that the Fe(III) cannot easily be reduced at the membrane surface. This is consistent with the observation above that only a small fraction of total membrane-bound ferrocene is electrochemically accessible. This suggests that the material may be used as a singular membrane matrix without the need for a more complex two-layer system that is necessary with the conducting polymer based ion to electron transducing layers.

One disadvantage of the conducting polymer layer POT as an ion-to-electron transducer appears to be its limited redox capacity. As shown by Kim et al., a layer of this polymer obtained during electro-deposition on a 5 mm diameter gold electrode and modified with a thin, spin-coated PVC membrane showed a capacity limit of about $3 \mu C$.²⁵ This value was found for a stripping voltammetry analysis applying 30, 60, 120, 300, and 600 s doping times. An analogous experiment was performed here for FcPVC-based electrode applying the same doping times at 0.8 V. Since the stripping process was expected to be slower for a thicker membrane (about $100 \mu m$), more suitable procedure for FcPVC redox-capacity study was to calculate the charge of a doping process applying chronoamperometry. The doping was performed at 0.8 V for 30, 60, 120, 300, and 600 s. The charge calculated based on integrals of obtained chronoamperograms is presented as a function of doping time in Figure 6. Contrary to results obtained by Kim et al. where the POT based electrode reached its maximum capacity after 2 min to a value of less than $3 \mu C$,²⁵ the doping charge was still growing for the FcPVC-based electrode after 600 s. It was found that after 600 s of FcPVC doping, the

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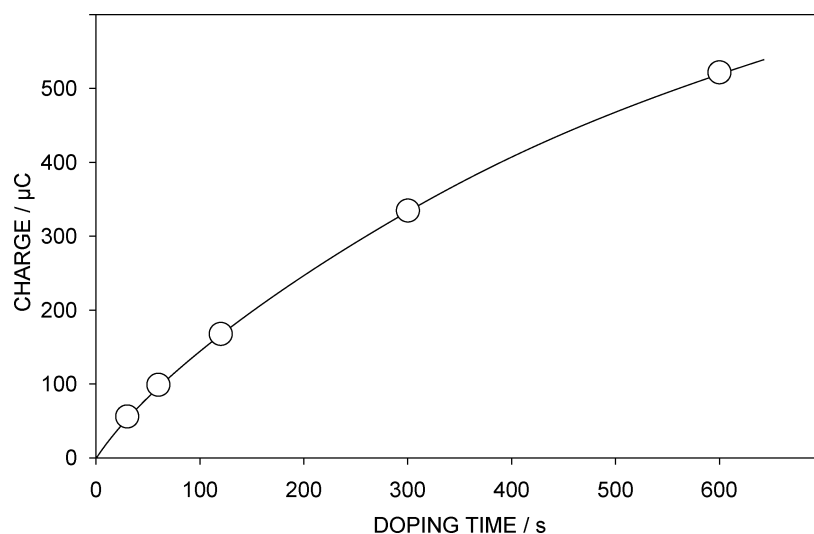


Figure 6. Calculated charge from chronoamperometric perchlorate ion uptake (0.1 M NaClO_4) into the ferrocene modified plasticized PVC membrane electrode, performed at 0.8 V vs Ag/AgCl and carried out for the indicated times.

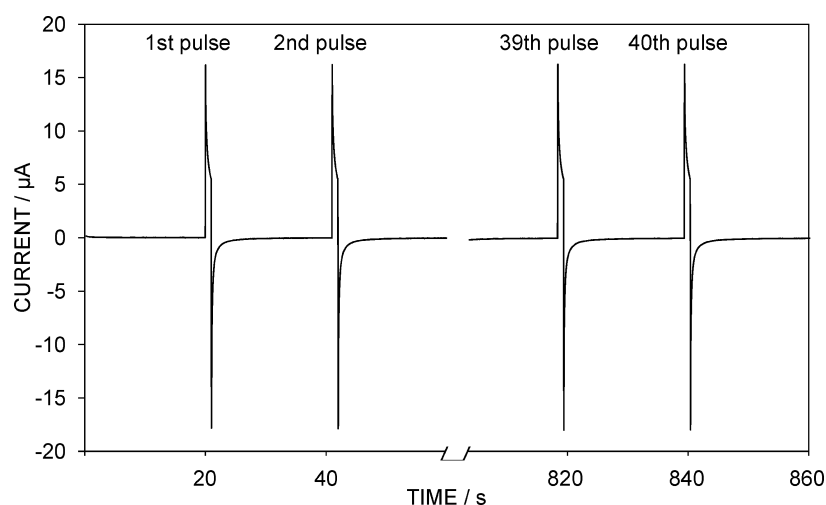


Figure 7. Normal pulse amperometry of a FcPVC-based membrane electrode immersed in 10 mM NaClO_4 for 40 anodic perchlorate ion transfer pulses for 1 s at 0.5 V, each followed by 20 s stripping pulses at 0.3 V (open circuit potential, found before the experiment). Shown here for clarity are the first and last two of the recorded pulses.

calculated doping charge was more than 520 μC , which is 2 orders of magnitude larger than for POT based electrodes. The value is somewhat larger than for the sandwiched system described above (see Figure 2), likely because of the applied electrochemical doping times were not long enough to effect conversion of the entire membrane material. Moreover, more than 50 μC conversion was observed for FcPVC in the first 30 s, significantly more than the 2.5 μC for POT-based membranes in the same time period,²⁵ which is advantageous for ion voltammetry sensor development.

When operating the membrane by normal pulse amperometry or normal pulse voltammetry, the observed currents are often limited by ion transport processes in the aqueous or membrane phase.⁴³ If this holds true, changes in charge transfer kinetics of the underlying redox couple may not substantially influence the observed amperometric response if the potential of the redox couple remains constant in the course of the experiment. Figure 7 demonstrates normal pulse amperometry in a 10 mM NaClO_4 solution, using a 1 s excitation pulse at 0.5 V followed by a 20 s baseline pulses at the open circuit potential. Indeed, the current response generated during the 1 s long pulse was very

reproducible (1% relative SD) in the course of a 40 pulse sequence. This suggests that the ferrocene modified PVC introduced here is a promising material for voltammetric ion sensor design. While we have not tested the behavior of freely dissolved lipophilic ferrocene species in this work, we note that the group of Samec has reported on adequate stability with membranes containing freely dissolved 1,1'-dimethylferrocene as a redox active additive, although possible interference by redox active species in the sample were not yet studied there.³⁰

CONCLUSIONS

This paper presented a modification of PVC with ferrocene groups via an attractive “click chemistry” approach. The new material (FcPVC) was characterized in view of membrane electrode applications, specifically with voltammetric transduction principles. A new method applying two identical electrodes at the same doping state sandwiched together allowed one to confirm the redox properties of the FcPVC, independent of the processes occurring at the sample side of the membrane. This is important because the resulting sensors are often operationally limited by

ion transfer and diffusion processes, which are not the focus of this research. The redox capacity of the system was found to correspond to several nanomolar of oxidizable ferrocene groups in the membrane, which is only a fraction of nominal ferrocene concentration. This suggests that the ferrocene groups are sufficiently dilute and immobile in the membrane and that it is the surface confined functionalities that are predominantly electrochemically accessible. Nonetheless, the redox capacity appears to be adequate for most voltammetric ion transfer applications. The membranes were characterized in contact with aqueous electrolytes, and interrogation with normal pulse voltammetry suggests excellent reproducibility and an anion selectivity pattern that corresponds to the expected Hofmeister selectivity sequence. The cathodic potential window remained featureless, supporting the notion of a membrane containing predominantly ferrocene moieties that can be oxidized by the concomitant extraction of anions from the sample. It is expected that adequate chemical doping of the membrane with cation-exchanger species will make the cationic response region at cathodic potentials analytically

accessible, but this was not yet explored here. Experiments in the presence of potassium hexacyanoferrate(III) showed that possible presence of ferrocene groups at the surface of the ion-selective membrane do not cause redox sensitivity of the electrode. Moreover, the high reproducibility of the sampled anion transfer currents (standard deviation below 1%) as well as the high redox capacity of the material (about 520 μC) makes ferrocene bound PVC an attractive material for electrochemical all solid state ion-selective electrode fabrication.

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