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2019

Arroyo, J., Akieh-Pirkanniemi, M., Lisak, G., Latonen, R.-M., & Bobacka, J. (2019).
Electrochemically controlled transport of anions across polypyrrole-based membranes.
Journal of Membrane Science, 581, 50-57. doi:10.1016/j.memsci.2019.02.028

<https://hdl.handle.net/10356/144154>

<https://doi.org/10.1016/j.memsci.2019.02.028>

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Electrochemically controlled transport of anions across polypyrrole-based membranes

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Declarations of interest: none.

Abstract

Electrosynthesized polypyrrole (PPy) films on PVDF/Pt support membranes were used to study electrochemically controlled transport of monovalent and divalent anions across the PPy-based membranes. The PVDF/Pt/PPy membrane separated two compartments in a transport cell and served simultaneously as the working electrode allowing electrochemical switching of PPy between its oxidized and reduced forms during the transport experiments. PPy was electrosynthesized in presence of p-toluene sulfonate, camphorsulfonate and hexafluorophosphate (doping ions) and the ion transport properties of the resulting PPy-based membranes were investigated. The morphology and elemental composition of PPy before and after the anion transport studies were studied by SEM and EDXA. The anion fluxes obtained during transport of a mixture of Cl^- , NO_3^- , SO_4^{2-} and HAsO_4^{2-} across the PPy-based membranes were found to decrease in the following order: $\text{NO}_3^- > \text{Cl}^- \gg \text{SO}_4^{2-} > \text{HAsO}_4^{2-}$. PPy films with the same composition as for the transport studies were also electrodeposited on glassy carbon electrodes (GC/PPy) and studied by potentiometry. The potentiometric selectivity of the GC/PPy electrodes towards Cl^- , NO_3^- and SO_4^{2-} was found to correlate with the ion transport characteristics of the corresponding PPy membranes used in the transport cell. The PPy-based membranes allowed separation of monovalent from divalent anions.

Keywords: Polypyrrole membrane; anion transport; selectivity; electrochemically controlled anion transport; anion separation.

1. Introduction

Conducting polymers (CPs) such as polypyrrole (PPy), polyaniline and polythiophene are attractive materials owing to their redox reversibility as well as their electrical and optical properties. These properties have been utilized in various applications, such as biosensors [1-3], electromechanical actuators [4], corrosion protection films [5, 6], batteries [7, 8], platforms for controlled release of drugs [9, 10], ion exchange materials [11-15] and selective bilayer transport membranes [16].

CPs are electroactive materials that are capable of exchanging anions and cations during oxidation and reduction of the polymer [17-20]. During oxidative polymerization, anions (dopants) are inserted into the CP film to compensate the positive charge on the CP backbone, i.e. to maintain electroneutrality of the film. When the same polymer is reduced, its backbone becomes electrically neutral and the doping anion is expelled to keep the overall electroneutrality of the film. In cases when the doping anion is immobile (trapped in the CP film), cations present in the electrolyte solution are inserted to maintain charge balance upon reduction of the CP. Further on, when the polymer is re-oxidized the backbone of the polymer recover its positive charge and cations that were inserted previously are expelled and anions from the electrolyte solution may be inserted as well. In this way, repeated oxidation/reduction of the CP activates the transport of ions to/from the CP film that can be utilized in functional membranes for uptake or release of ions.

Earlier studies have confirmed the influence of the doping ions in CPs on the transport of cations and anions [21-32]. If the doping anion is small and mobile such as Cl^- , ClO_4^- , NO_3^- or BF_4^- , the CP interacts primarily with anions, but under certain conditions, cation exchange may also occur. Strong interactions (even covalent bond formation) between certain dopants (Cl^- , F^-) and CPs (PEDOT, PPy) were reported by Tóth et al. [33, 34]. Contrary to expectations, cation exchange properties were observed for the CPs for these halide doping anions [33, 34]. Cation exchange is expected to dominate when the doping anion is large and immobile such as polyvinylsulfonate, sulfonated calixarene, polystyrenesulfonate and copper phthalocyaninetetrasulfonate. Medium size doping ions such as p-toluenesulfonate (pTS^-) and

dodecylbenzenesulfonate have been shown to result in transfer of both cations and anions during the charge compensation process [16].

Applying an electrical stimulus to the CP has thus been found to facilitate the transport of ions across a CP membrane [21]. During the doping process dramatic changes occur in the CP films, such as changes in hydrophilicity/hydrophobicity, volume change (swelling and shrinking) and variations in permselectivity [22]. Several factors, such as the size and charge of the doping ions have been shown to influence the transport of ions across CPs [35, 36]. Furthermore, the thickness of the deposited CP film [37] as well as the ions present in the electrolyte solution and its pH [38-40] may affect the movement of ions in CPs. A detailed understanding of the ion transport in CPs is of utmost importance for membrane applications of CPs.

This study targets the electrochemically stimulated transport of anions across PPy-based electroactive ion exchange membranes, which in contrast to conventional ion exchange membranes allow electrochemical switching of the membrane. Conventional ion exchange membranes are good ionic conductors due to the mobility of their exchangeable ions, but lack electronic conductivity and electroactivity [41]. The ability of CPs to act in electroactive ion exchange membranes involves absorption and desorption of ions through oxidation and reduction of the ion exchange material, i.e. electrochemically activated transport. This method does not require any additional chemicals (acids or bases) for generation of ion exchange sites and as a result, production of waste decreases significantly [42], which is one of the major advantages compared with conventional ion exchange resins. PPy has also been used as an additional layer on the surface of conventional ion exchange membranes in order to tune the ion transport selectivity [41,43]. For example, PPy synthesized by chemical oxidative polymerization using FeCl_3 as oxidant formed a dense layer on three different anion exchange membranes that decreased the permeability of urea [44]. Interestingly, PPy deposited on (or inside) anion-exchange membranes was found to decrease the transport number of sulfate relative to chloride ions [44].

The present work is focused on the transport of monovalent (Cl^- , NO_3^-) and divalent (SO_4^{2-} , HAsO_4^{2-}) anions across electroactive ion exchange PVDF/Pt/PPy membranes. Separation of the toxic HAsO_4^{2-} from other anions is of particular interest for practical applications. PPy was electropolymerized in presence of small-medium size anions, i.e. hexafluorophosphate (PF_6^-), pTS $^-$ and camphorsulfonate (CSA^-), to obtain PPy-based ion-exchange membranes with different morphologies and ion-transport properties. The aim of this study was to get a deeper

understanding of the electrochemically stimulated ion-transport properties of PPy-based membranes.

2. Experimental

2.1. Chemicals

Pyrrole was obtained from Sigma-Aldrich and distilled prior to use. The distilled pyrrole was tightly sealed in an argon environment and kept in the dark below 0 °C until further use. All other chemicals were used as received. Sodium hexafluorophosphate (NaPF_6), camphor-10-sulfonic acid (HCSA), NaNO_3 , Na_2SO_4 and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ were purchased from Sigma-Aldrich. (*NOTE: arsenic compounds are toxic if swallowed, or if inhaled, may cause cancer, are very toxic to aquatic life and have long lasting effects to aquatic life.*) Toluene-4-sulfonic acid monohydrate ($\text{HpTS} \cdot \text{H}_2\text{O}$) and NaCl were purchased from Fluka. Deionised water (18 M Ω cm) was produced by a PureLAB Ultra (ELGA) system and used to prepare the solutions. Polyvinylidene difluoride (PVDF, Millipore, average pore size 0.22 μm and thickness 100 μm), sputter-coated with Pt, was used as support material for deposition of the PPy films.

2.2. Membrane Preparation

A thin layer of Pt was deposited on the PVDF membrane using a BAL-TEC SCD 050 sputter coater operating at 40 mA for 450 s. This was performed to render the PVDF/Pt membrane electrically conductive, allowing electrodeposition of PPy to obtain PVDF/Pt/PPy membranes and allowing electrochemical switching of PPy in the resulting PVDF/Pt/PPy membrane. PPy was doped with three different doping ions, namely pTS^- , CSA^- and PF_6^- . In all cases, the polymerization solution consisted of 0.20 M pyrrole, and either 0.05 M HpTS, 0.05 M HCSA or 0.1 M NaPF_6 . All polymerization solutions were deoxygenated with argon gas prior to polymerization. Galvanostatic electropolymerization was performed in all instances by applying a constant current density to the PVDF/Pt working electrode in the polymerization solution with an Autolab PGSTAT 20 potentiostat/galvanostat. A current density of 1 mA cm^{-2} was applied for 15 min for the PPy(pTS) film and for 30 min for the PPy(CSA) film. For the PPy(PF_6) film a current density of 2 mA cm^{-2} was applied for 40 min.

Polymerization was performed in a two-electrode cell consisting of the PVDF/Pt membrane working electrode (area = 7.07 cm^2) contacted with a platinum wire and a glassy carbon (GC) rod as the counter electrode. After electropolymerization of PPy, the PVDF/Pt/PPy membranes were washed thoroughly with deionized water in order to remove any remaining monomer,

oligomers and electrolyte salt. The same membranes which were used in the transport studies were also investigated by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDXA).

2.3. Transport Studies

After electropolymerization the PVDF/Pt/PPy membranes were soaked in 50% ethanol-water for ca 30 s in order to increase the hydrophilicity of the PVDF membrane. After that the membrane was assembled in the transport cell. A freshly prepared membrane was used for each transport experiment. The transport cell consisted of two compartments separated by the membrane as illustrated in Figure 1.

To study the transport of anions, 2.5 mL of each 0.1 M anion (Cl^- , NO_3^- , SO_4^{2-} , HAsO_4^{2-}) solution was poured and mixed into the source cell, while 10 mL of deionized water was poured into the receiving cell. Each cell compartment contained an Ag/AgCl (3 M NaCl) electrode as the reference electrode and a GC rod as the counter electrode. Both counter electrodes were used at the same time in each cycle during the repeated oxidation and reduction of the polymer membrane, i.e. the two counter electrodes were connected together and the two reference electrodes were connected together. The PVDF/Pt/PPy membrane worked as a common working electrode for both cell compartments.

To investigate whether the anion flux across the membrane can be electrochemically controlled or not, the transport experiments were performed in three stages. In stage 1 (region A), no potential was applied to the membrane for 1 h. In stage 2 (region B), a pulsed potential waveform was applied to the membrane for 2 h. During this stage, the membrane was first subjected to -0.8 V for 50 s, and then immediately switched to +0.5 V for another 50 s, after which the cycle was repeated for the next 2 h. In stage 3 (region C), no potential was applied to the membrane for 1 h. Altogether, the experiment lasted for 4 h and during this time 1 mL aliquot was withdrawn every 30 minutes from the receiving cell to determine the concentration of anions. To maintain a constant volume in the receiving cell, 1 mL of deionized water was added for each 1 mL aliquot that was withdrawn. To determine the anion concentrations, the samples were analyzed with ion chromatography (IC) and inductively coupled plasma optical emission spectrometry (ICP-OES).

Fig. 1. Schematic illustration of the transport cell, CE: counter electrode, RE: reference electrode, WE: working electrode. A^{x-} represents the anion under study.

2.4. Ion Chromatography

The concentrations of Cl^- , NO_3^- and SO_4^{2-} anions in the receiving solution were determined by IC using a 761 compact IC 1.1 instrument (Metrohm AG, Switzerland) connected to a conductivity detector. 20 μL of the sample was injected into the separator column (Metrosep anion Dual 2). Three replicates of each sample were measured. The eluent consisted of a mixture of 2 mM NaHCO_3 and 1 mM Na_2CO_3 pumped at a flow rate of 0.8 mL min^{-1} . A Metrohm Suppressor Module (MSM) was used to enhance the sensitivity of the anion detection. 0.1 M H_2SO_4 was used for regeneration of the suppressor and deionized water was used for washing it.

2.5. ICP-OES measurements

A Perkin Elmer Optima 5300 DV ICP-OES instrument was used to determine the concentration of arsenic (As) in the receiving solution. The following instrumental parameters were set for the concentration measurements: nebulizer flow = 0.8 L min^{-1} , auxiliary gas flow = 0.2 L min^{-1} , plasma gas flow = 15 L min^{-1} and plasma power = 1300 W. For the determination of arsenic, axial viewing of the plasma was employed. The concentration of arsenic reported in this study was determined using the emission wavelength of 188.979 nm. A multi-element standard was

used as the calibration solution and the samples were diluted by a factor of 4 prior to the ICP-OES measurements.

2.6.SEM measurements

The morphology and the film thickness of the composite membranes were determined with a Leo 1530 Gemini scanning electron microscope having a ThermoScientific Ultra Dry x-ray detector. The membrane thickness was determined from the cross sections of freshly prepared PVDF/Pt/PPy membranes. Elemental analysis was carried out using Energy Dispersive X-ray Analysis (EDXA) and the images were recorded simultaneously.

2.7. Selectivity studies

In addition to the membrane transport studies, ion-selectivity studies were performed by potentiometric measurements using PPy electrodeposited on glassy carbon (GC) disk electrodes (area = 0.07 cm²). The separate solution method (SSM) was used to determine the selectivity coefficients, assuming chloride as the primary ion. The GC electrodes were polished using 0.3 μm Al₂O₃ powder, and washed with deionized water. The current and charge applied to the electrodes during electropolymerization of pyrrole was recalculated according to the lower surface area of the GC disk electrodes compared to the PVDF/Pt substrates, but the electropolymerization was otherwise performed according to the same procedure as described in Section 2.2. Three GC/PPy electrodes were prepared and used for each doping ion. The potentiometric measurements were performed by registering the open-circuit potentials of the electrodes in solutions of various anion concentrations (from 2.5×10⁻¹ M to 2.5×10⁻⁴ M). The obtained calibration curves for GC/PPy(pTS), GC/PPy(CSA) and GC/PPy(PF₆) electrodes in the primary (Cl⁻) and interfering anion (NO₃⁻, SO₄²⁻, HAsO₄²⁻) solutions were used to calculate the selectivity coefficients. The uncertainties in the selectivity coefficients were obtained by measuring three replicates with three GC/PPy electrodes for each doping ion. During the measurements, the electrochemical cell was placed inside a Faraday cage. All experiments were performed at room temperature (20-21 °C).

3. Results and Discussion

3.1.Morphological characterization and membrane thickness

The morphology of the composite membranes used in the anion transport studies was examined by SEM. The PVDF/Pt membranes, on top of which the PPy films were deposited, present an irregular network with an average pore size of 0.22 μm. Figure 2 shows the SEM images from

the surface of the PPy membranes with pTS^- , CSA^- and PF_6^- ions used as dopants before and after the transport studies and Figure 3 shows the SEM images from the cross-sections of the PVDF/Pt/PPy membranes after the transport studies. The layer of Pt is not clearly evident in the three cross-section images due to the fact that during sputtering Pt is deposited into the bulk of the PVDF matrix. During sputtering of Pt on the PVDF membrane, a thin layer of Pt is deposited on the surface of PVDF as well as along the walls of the pores. Platinum deposited on the walls of the pores makes it possible for polymerization of Py to occur inside the pores as well [45, 46].

In general, the morphology of the films did not change after they had been used in the transport studies. The PPy(pTS) membrane shows a dense, compact layer with some spikes, which is typical for the PPy(pTS) [16]. The PPy(CSA) membrane shows a slightly porous structure and the PPy(PF_6) membrane has a “cauliflower-like” structure.

Fig. 2. SEM images of PPy composite membranes: view perpendicular to the surface of PPy(pTS), PPy(CSA) and PPy(PF_6) (a) prior to a transport study and (b) after a transport study.

Table 1 compares the theoretical thicknesses of the dry PPy films based on the charge consumed during polymerization, with the experimental thicknesses determined from the SEM images of the cross- sections of the composite membranes shown in Figure 3. The theoretical thickness of the dry polymer film, l , was calculated according to Eq. (1) [45].

$$l = \left(\frac{QM}{nFA\rho} \right) \quad (1)$$

In this equation, Q represents the amount of charge consumed during polymerization, M is the molecular mass of the monomer, n is the number of electrons involved in the polymerization reaction and doping (assumed to be 2.3, i.e. 2 e⁻ per monomer unit for coupling and 0.3 e⁻ per monomer unit to dope the PPy film to 30%), A is the area of the electrode, F is the Faraday constant and ρ is the density of the film (approximated to 1 g cm⁻³).

Table 1. Calculated and measured thicknesses of PPy films doped with pTS⁻, CSA⁻ and PF₆⁻ ions deposited on the PVDF support material under galvanostatic conditions. The measured thickness considers only the dense part of the film.

Polymer	Current density (mAcm ⁻²)	Growth time (min)	Calculated thickness (μm)	Measured thickness (μm)
PPy(pTS)	1	15	2.7	3.2
PPy(CSA)	1	30	5.4	5.8
PPy(PF ₆)	2	40	14.5	7.2 ^a

^a The compact layer (7.2 μm) is covered with humps (30μm).

There is a relatively good agreement between the calculated and measured thickness values for PPy(pTS), PPy(CSA) and PPy(PF₆) membranes, when taking into account that the thickness of the PPy films shows some variations due to spikes and humps (Figure 3). As can be seen in Figure 3, PPy(PF₆) shows a compact later covered with large humps, which makes it difficult to estimate the experimental thickness from the SEM micrograph.

Fig. 3. SEM micrographs from the cross-sections of (a) the PVDF/Pt-PPy(pTS) membrane, (b) the PVDF/Pt-PPy(CSA) membrane and (c) the PVDF/Pt-PPy(PF₆) membrane after the transport.

3.2. Anion transport studies

Figure 4 shows the results from transport studies of equimolar concentrations of anions (Cl^- , NO_3^- , SO_4^{2-} and HAsO_4^{2-}) present simultaneously in the source cell. These experiments were conducted with all the studied PPy(pTS), PPy(CSA) and PPy(PF₆) membranes using the same electrochemical stimulation procedure which was divided in three regions. In region A, no potential was applied to the membrane. In region B, a pulsed potential waveform with potential limits of -0.8 and +0.5 V with a pulse width of 50 s was applied. In region C, no potential was applied.

As can be observed in Figure 4a, no transport of either mono- or divalent anions was observed during region A through the PPy(pTS) composite membrane. When the electrical stimulus was applied on the membrane, transport of monovalent anions took place while the divalent anions did not cross the membrane. When the electrical stimulus was stopped, the flux of monovalent anions levelled off gradually. This “levelling-off” phenomenon in region C agrees well with earlier transport studies of NO_3^- through PPy(pTS). Akie et al. [46] have shown that PPy(pTS) presents permeability towards both cations and anions (K^+ , Ca^{2+} , NO_3^-). Therefore, anions (and cations) accumulated in PPy(pTS) may be slowly released into the receiving cell solution even in the absence of an electrical stimulus. However, in absence of any electrical stimulus, the flux of anions in region C eventually stops. The same effect is observed for the PPy(CSA) and PPy(PF₆) conductive composite membranes (Figures 4b and 4c) in the case of Cl^- and NO_3^- . Interestingly, SO_4^{2-} and HAsO_4^{2-} are not transported through PPy(pTS) when the other anions are also present in the source solution (Figure 4a), this indicates that PPy(pTS) shows selective transport of monovalent anions in presence of divalent ones.

Electrolysis of water plays a key role for the ion compensation during oxidation and reduction of the polymer [46]:

These reactions can donate either OH^- anions or H^+ cations into the source and receiving solutions, which are needed to maintain macroscopic electroneutrality in the transport cell. Thus H^+ produced in the receiving cell can compensate for the anions transported into the receiving cell solution during the course of the experiments.

It can be seen in Figure 4 that PPy(pTS), PPy(CSA) and PPy(PF₆) show selective transport of monovalent anions (Cl⁻, NO₃⁻) over divalent ones (SO₄²⁻, HAsO₄²⁻) in mixed solutions and the flux can be controlled electrochemically. The shape of the studied anions is remarkably different from each other, because Cl⁻ is spherical and NO₃⁻ is planar, while SO₄²⁻ and HAsO₄²⁻ are tetrahedral [47,48]. Therefore, in addition to the charge, also the geometry of the anions used in this study can influence the transport through the membranes in these studies.

In addition to their charge and size/geometry [47-49], the limited transport of divalent ions like SO₄²⁻ can also be related to the Gibbs hydration energy ($-\Delta G_h^0$) [41-43], which is 1000 kJ mol⁻¹ for SO₄²⁻ as compared with 270 kJ mol⁻¹ for NO₃⁻ and 317 kJ mol⁻¹ for Cl⁻ [42]. The $-\Delta G_h^0$ of SO₄²⁻ is about three times larger than that of Cl⁻ and NO₃⁻ ions, leading to a strongly hydrated SO₄²⁻ anion that does not easily permeate through the membrane. Thus, during transport of mono- and divalent anions in a PPy based membrane, the movement of monovalent anions is dominant.

As it is shown in Figure 4b the transport of monovalent anions in the PPy(CSA) membrane is more than five times higher compared with the transport of monovalent anions in the PPy(pTS) and PPy(PF₆) membranes. A slight transport of divalent anions was also observed for the PPy(CSA) membrane compared to almost no transport with the other membranes. The reasons for the higher overall transport rate for PPy(CSA) is not clear at the moment. We can only speculate that membrane porosity as well as differences in transport numbers for anions relative to cations may play their roles here.

Fig. 4. Transport profiles for a mixture of Cl⁻, NO₃⁻, SO₄²⁻ and HAsO₄²⁻ across (a) PPy(pTS) membrane, (b) PPy(CSA) membrane and (c) PPy(PF₆) membrane. For all experiments, the source solution contained an equimolar concentration (0.025 M) of NaCl, NaNO₃, Na₂SO₄ and Na₂HAsO₄. Region (A): no potential is applied, (B): pulsed potential waveform is applied (-0.8V to +0.5V, 50s) and (C): no potential is applied.

The flux, F , of the anions across the composite membranes was calculated at the end of region B of the transport experiment, using Eq. (2) [45]:

$$F = \frac{n}{t A} \quad (2)$$

Where n is the number of moles of anions, t is the total time spent in region B of the experiment and A is the area of the membrane exposed to the receiving solution ($A = 7.07 \text{ cm}^2$). The calculated anion fluxes are given in Table 2. As can be seen in the table the anion flux decreases for PPy(pTS) and PPy(CSA) membranes according to the following sequence $\text{NO}_3^- > \text{Cl}^- \gg \text{SO}_4^{2-} > \text{HAsO}_4^{2-}$, while the PPy(PF₆) membrane was more permeable to Cl^- than NO_3^- and practically impermeable to the divalent anions. This supports the conclusion that the transport of monovalent anions is dominant compared to divalent anions.

Table 2: Anion fluxes obtained from the transport of a mixture of Cl^- , NO_3^- , SO_4^{2-} and HAsO_4^{2-} across the PPy based composite conducting membranes.

Anion	Flux ($\times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$)		
	PPy(pTS)	PPy(CSA)	PPy(PF ₆)
Cl^-	0.24	1.33	0.45
NO_3^-	0.71	1.74	0.39
SO_4^{2-}	0	0.11	0
HAsO_4^{2-}	0	0.06	0

3.3. Elemental analysis of the studied membranes

The results of elemental analyses obtained before and after the use of the membranes in the transport studies are presented in Table 3. Sulfur is originating exclusively from the pTS⁻ and CSA⁻ doping anions and phosphorus from the PF₆⁻ dopant. The other elements originate from polypyrrole and any ions from the source cell. During the transport experiments, the source cell contained an equimolar mixture of anions (Cl^- , NO_3^- , SO_4^{2-} and HAsO_4^{2-}). The carbon and nitrogen content of the PPy(pTS) membrane before the transport experiment originates from PPy. After the transport experiments, the amount of nitrogen in the PPy(pTS) membrane increased slightly (2.2 %) while the amount of oxygen and sulfur (originating from the pTS⁻

doping ions) decreased. This indicates that part of pTS^- in PPy(pTS) was replaced by NO_3^- during the transport experiment.

Analogously, the amount of nitrogen in PPy(CSA) increased while the amount of oxygen and sulfur (originating from the CSA^- doping ions) decreased after the transport experiment. This again indicates that part of CSA^- in PPy(CSA) was replaced by NO_3^- during the transport experiment.

Table 3. Results from EDX elemental analysis of the PPy composite membranes before and after a transport experiment, when the source solution contained an equimolar concentration of NaCl , NaNO_3 , Na_2SO_4 and Na_2HAsO_4 .

Polymer	Before transport (atom (%))						After transport (atom (%))					
	C	N	O	S	F	P	C	N	O	S	F	P
PPy(pTS)	68.0	12.9	13.7	4.6	nd	nd	67.9	15.1	11.8	3.5	nd	nd
PPy(CSA)	63.5	17.7	15.3	3.9	nd	nd	63.1	19.4	13.9	3.3	nd	nd
PPy(PF ₆)	51.4	14.9	3.0	nd	25.3	5.2	58.8	20.1	4.9	nd	12.3	3.1

nd: not determined

Oxygen observed in the elemental analysis in the $\text{PPy(PF}_6\text{)}$ membrane before the transport experiment may originate from absorbed water in the polymer film due to washing of the membrane with 50% ethanol- H_2O solution. As can be seen in Table 3, the amount of nitrogen and oxygen in the $\text{PPy(PF}_6\text{)}$ membrane increased while the amount of fluorine and phosphorous (originating from the PF_6^- doping ions) decreased after the transport experiment. This indicates once more that part of the original doping ions (PF_6^-) in $\text{PPy(PF}_6\text{)}$ was replaced by NO_3^- during the transport experiment.

The elemental analyses of all PPy membranes studied showed that also Cl^- enters the membrane after the transport experiments. To some extent, the same phenomenon may occur also with the other anions, but it is more visible for Cl^- and NO_3^- . However, the contribution of Cl^- to the total element content in the membranes was less than 1%, which is the reason why it is not shown in Table 3.

Fig.5. Potentiometric response of GC/PPy(pTS), GC/PPy(CSA) and GC/PPy(PF₆) electrodes for different concentrations of Cl^- , NO_3^- , SO_4^{2-} and HAsO_4^{2-} anions.

3.4. Selectivity studies of the composite membranes

In order to study the selectivity of the PPy membranes, potentiometric measurements were performed for GC/PPy electrodes assuming Cl^- as the primary (i) ion and the other anions studied as interfering (j) ions. The selectivity coefficients were calculated according to the Nikolskii-Eisenman equation, Eq. (3) [50]:

$$\log K_{i,j}^{pot} = \frac{z_i F}{2.303 RT} (E_j^{0'} - E_i^{0'}) = \frac{z_i F}{2.303 RT} (E_j^{EMF} - E_i^{EMF}) \log \frac{a_i}{a_j^{z_i/z_j}} \quad (3)$$

where z_i and z_j are the charges, and a_i and a_j are the activities of the primary and the interfering ion, respectively; and R , T and F have their usual electrochemical significance. E_i^{EMF} and E_j^{EMF} are the measured potentials in the solutions of i and j , respectively. Figure 5 shows the potentiometric response of PPy(pTS), PPy(CSA) and PPy(PF₆) electrodes for the anions investigated in this study.

As can be seen in Figure 5, the GC/PPy electrodes gave a linear (Nernstian) response for Cl^- , NO_3^- and SO_4^{2-} , while the response for HAsO_4^{2-} was nonlinear. Therefore, the slopes and selectivity coefficients were obtained only for Cl^- , NO_3^- and SO_4^{2-} . The observed slopes and the selectivity coefficients obtained by the separate solution method (SSM) for the GC/PPy(pTS), GC/PPy(CSA) and GC/PPy(PF₆) electrodes are shown in Table 4. As can be seen in Table 4, the electrodes show a close to Nernstian slope for Cl^- , NO_3^- and SO_4^{2-} .

Table 4: The observed calibration slopes and selectivity coefficients obtained according to the separate solution method (SSM) for PPy(pTS), PPy(CSA) and PPy(PF₆). The standard deviations of the measurements were obtained from measurements with three identical electrodes.

	Cl^-	SO_4^{2-}		NO_3^-	
	Slope (mV/dec)	Slope (mV/dec)	log K	Slope (mV/dec)	log K
PPy(pTS)	-56.0 ± 0.5	-27.3 ± 3.6	-0.68 ± 0.2	-57.0 ± 1.3	-0.13 ± 0.05
PPy(CSA)	-56.2 ± 3.2	-27.3 ± 1.2	-0.72 ± 0.2	-56.4 ± 2.2	-0.20 ± 0.06
PPy(PF ₆)	-58.8 ± 2.0	-25.7 ± 6.3	-1.83 ± 0.2	-61.8 ± 0.8	-0.17 ± 0.07

All GC/PPy electrodes studied showed higher potentiometric selectivity for Cl^- and NO_3^- than for SO_4^{2-} . This is in agreement with results from the transport studies (Figure 4), which show preference for Cl^- and NO_3^- over SO_4^{2-} . Unfortunately, a direct comparison between the transport of HAsO_4^{2-} and its potentiometric selectivity was not possible due to the non-Nernstian response of GC/PPy towards HAsO_4^{2-} (Figure 5).

4. Conclusions

The monovalent anions, Cl^- and NO_3^- , were preferably transported through membranes based on PPy(pTS), PPy(CSA) and PPy(PF₆) films during electrochemical switching of PPy. The divalent anions, SO_4^{2-} and HAsO_4^{2-} , were more difficult to transport through the PPy-based membranes, even if a pulsed potential was applied to the conductive polymer membrane. Elemental analysis indicated that the original doping ions (pTS⁻, CSA⁻ and PF₆⁻) in PPy were partly replaced by nitrate and to some extent by chloride, which were effectively transported through the PPy membrane during transport studies. The preferential transport of monovalent anions through PPy(pTS), PPy(CSA) and PPy(PF₆) membranes was related to the charge, size, geometry and Gibbs hydration energy of the studied anions. The calculated anion fluxes obtained after transport of a mixture of Cl^- , NO_3^- , SO_4^{2-} and HAsO_4^{2-} across the PPy-based membranes decreased in the following order: $\text{NO}_3^- > \text{Cl}^- \gg \text{SO}_4^{2-} > \text{HAsO}_4^{2-}$. This result correlated with the potentiometric selectivity of GC/PPy for NO_3^- , Cl^- and SO_4^{2-} anions. These results indicate that PPy-based membranes can be used to separate the highly toxic HAsO_4^{2-} from NO_3^- and Cl^- .

Acknowledgements

This work is part of the activities of the Johan Gadolin Process Chemistry Centre at Åbo Akademi University.

5. References

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Table 1. Calculated and measured thicknesses of PPy films doped with pTS⁻, CSA⁻ and PF₆⁻ ions deposited on the PVDF support material under galvanostatic conditions. The measured thickness considers only the dense part of the film.

Polymer	Current density (mAcm⁻²)	Growth time (min)	Calculated thickness (μm)	Measured thickness (μm)
PPy(pTS)	1	15	2.7	3.2
PPy(CSA)	1	30	5.4	5.8
PPy(PF ₆)	2	40	14.5	7.2 ^a

^a The compact layer (7.2 μm) is covered with humps (30μm).

Table 2: Anion fluxes obtained from the transport of a mixture of Cl^- , NO_3^- , SO_4^{2-} and HAsO_4^{2-} across the PPy based composite conducting membranes.

Anion	Flux ($\times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$)		
	PPy(pTS)	PPy(CSA)	PPy(PF ₆)
Cl^-	0.24	1.33	0.45
NO_3^-	0.71	1.74	0.39
SO_4^{2-}	0	0.11	0
HAsO_4^{2-}	0	0.06	0

Table 3. Results from EDX elemental analysis of the PPy composite membranes before and after a transport experiment, when the source solution contained an equimolar concentration of NaCl, NaNO₃, Na₂SO₄ and Na₂HAsO₄.

Polymer	Before transport (atom (%))						After transport (atom (%))					
	C	N	O	S	F	P	C	N	O	S	F	P
PPy(pTS)	68.0	12.9	13.7	4.6	nd	nd	67.9	15.1	11.8	3.5	nd	nd
PPy(CSA)	63.5	17.7	15.3	3.9	nd	nd	63.1	19.4	13.9	3.3	nd	nd
PPy(PF ₆)	51.4	14.9	3.0	nd	25.3	5.2	58.8	20.1	4.9	nd	12.3	3.1

nd: not determined

Table 4: The observed calibration slopes and selectivity coefficients obtained according to the separate solution method (SSM) for PPy(pTS), PPy(CSA) and PPy(PF₆). The standard deviations of the measurements were obtained from measurements with three identical electrodes.

	Cl ⁻	SO ₄ ²⁻		NO ₃ ⁻	
	Slope (mV/dec)	Slope (mV/dec)	log K	Slope (mV/dec)	log K
PPy(pTS)	-56.0 ± 0.5	-27.3 ± 3.6	-0.68 ± 0.2	-57.0 ± 1.3	-0.13 ± 0.05
PPy(CSA)	-56.2 ± 3.2	-27.3 ± 1.2	-0.72 ± 0.2	-56.4 ± 2.2	-0.20 ± 0.06
PPy(PF ₆)	-58.8 ± 2.0	-25.7 ± 6.3	-1.83 ± 0.2	-61.8 ± 0.8	-0.17 ± 0.07

Fig. 1. Schematic illustration of the transport cell, CE: counter electrode, RE: reference electrode, WE: working electrode. A^{x-} represents the anion under study.

Fig. 2. SEM images of PPy composite membranes: view perpendicular to the surface of PPy(pTS), PPy(CSA) and PPy(PF₆) (a) prior to a transport study and (b) after a transport study.

Fig. 3. SEM micrographs from the cross-sections of (a) the PVDF/Pt-PPy(pTS) membrane, (b) the PVDF/Pt-PPy(CSA) membrane and (c) the PVDF/Pt-PPy(PF₆) membrane after the transport.

Fig. 4. Transport profiles for a mixture of Cl^- , NO_3^- , SO_4^{2-} and HAsO_4^{2-} across (a) PPy(pTS) membrane, (b) PPy(CSA) membrane and (c) PPy(PF₆) membrane. For all experiments, the source solution contained an equimolar concentration (0.025 M) of NaCl, NaNO₃, Na₂SO₄ and Na₂HAsO₄. Region (A): no potential is applied, (B): pulsed potential waveform is applied (-0.8V to +0.5V, 50s) and (C): no potential is applied.

Fig.5. Potentiometric response of GC/PPy(pTS), GC/PPy(CSA) and GC/PPy(PF₆) electrodes for different concentrations of Cl^- , NO_3^- , SO_4^{2-} and HAsO_4^{2-} anions.

Highlights:

- Anion transport through polypyrrole membranes was controlled electrochemically
- Polypyrrole membranes separate monovalent anions from divalent anions
- Ion transport correlated with potentiometric selectivity for Cl^- , NO_3^- and SO_4^{2-}
- Polypyrrole membranes can separate the toxic HAsO_4^{2-} from NO_3^- and Cl^-