Controlled exchange of metallic cations by polypyrrole-based resins

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Abstract

Binding and release of various cations by polarization of polypyrrole based exchange-resins has been studied. The reversibility of the process has been investigated by electrochemical and nuclear techniques. It clearly depends on both the exchanged-cation and the sulfonated doping-ion. The selectivity of the process has also been analyzed by binding experiments from a mixture of two cations.

Keywords: Ion-exchange resin; Polypyrrole; Metallic cation; Electrochemical control

1. Introduction

Treatment of liquid waste is nowadays a great concern that requires the implementation of technologies based, e.g. on the binding and release of metallic cations. In this respect, the availability of ion exchange resins that can be stimulated by electrical potential is very attractive. Polypyrrole (PPy) doped by polyelectrolyte, such as polystyrene sulfonate ($PSSO_3$), is an example of cationic resin [1] that can electrochemically exchange stable cations, such as La^{3+} and Th^{4+} [2]. These cations are fixed when the polymer is reduced in relation to the quantity of reduction current. The reversibility of the process is however limited, an important part of Th and La being detected on the reoxidized resin.

This paper aims at studying the effect of the cation charge on the reversibility of the cation exchange. Purposely, monovalent (Cs^+) and bivalent (Ba^{2+}) cations will be compared with the previously analyzed La^{3+} and Th^{4+} cations. Moreover, it is worth investigating the ability of PPy resin to exchange $^{137}Cs^+$ which is a long half-life cation found in radioactive waste [3] and radioactive $^{140}Ba^{2+}$, which is also found in waste as fission products. Fixation of Co^{2+}, which is a less electrochemically stable cation found in the dismantling of nuclear power plants will also be considered [3].

The question of the possible role of the polyelectrolyte in the limited reversibility of the cation exchange will also be addressed. The polyelectrolyte will be replaced by a monofunctional dopant, i.e. heptanesulfonate ($HeptSO_3$), the expectation being that each dopant sulfonate will act as counter-ion of the polycationic polypyrrole [4], which is not obviously the case for the polyelectrolyte.

Similarly, monofunctional styrene sulfonate ($StySO_3$) will also be used as dopant [5], not only because it is a valuable model for the polymeric dopant but also because it could react with the PPy resin (during or after electropolymerization) so leading to the irreversible incorporation of the dopant.

Finally, some qualitative results will be collected about the fixation selectivity in a mixture of two cations of different charge [6].

2. Experimental

PPy/$PSSO_3$, PPy/$HeptSO_3$ and PPy/$StySO_3$ were synthesized by potentiometry (*E*=+0.7 V/SCE) onto carbon or platinum electrodes, in aqueous solution of pyrrole (0.1 M) and $PSSO_3Na$ (MW=70000, Aldrich), heptanesulfonate and styrenesulfonate sodium salts, respectively. The salt concentration was 0.1 M. The electrodeposited films were rinsed with twice-distilled water and analyzed in decimolar solutions of $ThCl_4$, $LaCl_3$, $BaCl_2$, $CoCl_2$ and $CsCl$ using the M270 EG&G PAR potentiostat/galvanostat. The electrochemical quartz crystal microbalance (QCM) [7] was used to measure mass changes of a Pt electrode by monitoring the resonance frequency of an AT-cut quartz crystal (Inficon; 0.2 cm^2) oscillating at 9 MHz.

Radioactive thorium cations were detected by an α-counter (VEMI PM/6305/type 6099B) working at 1240 V. Rutherford backscattering technique (RBS) [2 ; 8] (incident beam: 2.5 MeV α particles) and scanning electron microscopy (SEM) coupled with electron diffraction analysis of X-rays (EDAX) were used to detect non-radioactive cations.

3. Results and discussion

### 3.1. Polypyrrole/polystyrenesulfonate resin (PPy/PSSO$_3$)

Well-defined reduction and reoxidation peaks of the PPy/PSSO$_3$ polymer resin are observed by cyclic voltammetry whatever the cation in solution (Cs$^+$, Ba^{2+}, La^{3+}, Th^{4+}) (Fig. 1a, curves A and B). Since these four cations to be fixed have very cathodic reduction potentials, they cannot be reduced in water, and thus they do not react during the polymer reduction.

When the Co^{2+} cations are concerned, reduction to Co metal starts at −0.85 V/SCE in water onto C. When a C/PPy/PSSO$_3$ film is the electrode and the potential is slowly scanned down to −l V, the polymer reduction is observed at −0.3 V/SCE followed by the Co^{2+} reduction which is emphasized by a nucleation phenomenon (curve crossing) and the important stripping peak at −0.2 V (Fig. 1b, curve C). The application of a potential jump from the equilibrium potential to −l V leads to Co metal deposition rather than PPy reduction. An important stripping peak can then be observed during the anodic scanning. In contrast, Co^{2+} cations are fixed without reduction when the potential is scanned slowly from the equilibrium potential to −0.7 V (Fig. 2). The QCM analysis shows a mass increase during the cathodic scan as result of the polymer reduction and the simultaneous Co^{2+} incorporation. During reoxidation, the partial release of the cations is observed to occur.

The analysis of the RBS spectra for two PPy/PSSO$_3$ films (Q_s=l C) reduced to the same extent (Q_r=l6 mC) in CoCl$_2$ at −0.7 and −0.95 V, respectively, shows that the same amount of Co has been fixed by PPy (Fig. 3a). The S/Co atomic ratio has been evaluated to 0.2 with a superficial incorporation of Co (50 nm). Since Co (m) cannot be deposited at −0.7 V, the Co^{2+} fixation by the reduced PPy is thus confirmed, the fixation yield being the same at this lower potential than at −0.95 V. The dynamic fixation of this electroactive cation by PPy/PSSO$_3$ resin can thus be achieved by the careful control of the potential.

When the voltammetric scan of solutions containing Cs$^+$, Ba^{2+}, or La^{3+} is repeated, curve can be superimposed, stating that the polymer redox process is reproducible (Fig. 1a, curve A). Moreover, dependence of the maximum intensity of the anodic wave on the scanning rate is linear, which is the usual behavior of species that are precipitated on the electrode surface, such as conducting polymers. However, the intensity of the redox peaks changes with the exchanged cation: a higher intensity is observed in case of the monovalent Cs$^+$ cation compared to the multivalent cations (Ba^{2+}, La^{3+}) (Fig. 1a, curve B).

In case of ThCl$_4$ solution, the intensity of both the reduction and the oxidation peaks decreases when scans are repeated, supporting that the exchange of Th^{4+} is not totally reversible.
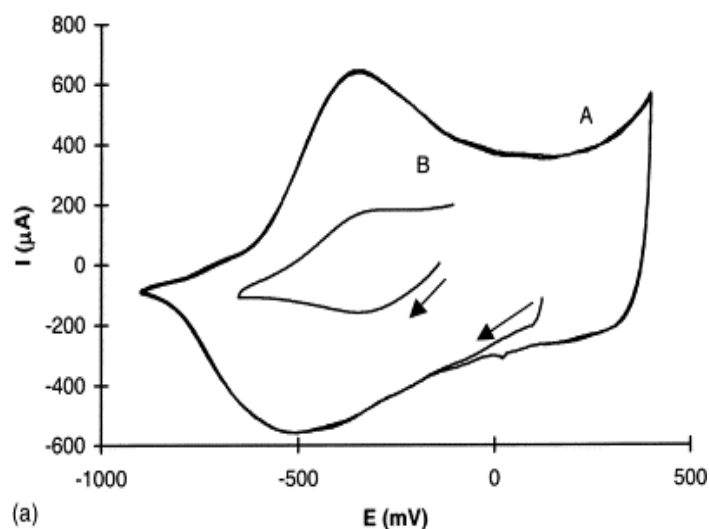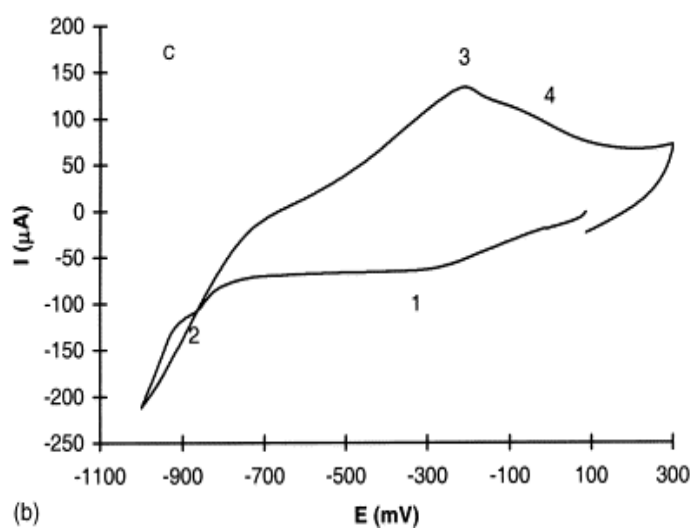
Fig. 1. Cyclic voltammograms for PPy/PSSO₃ film in aqueous solution of (a) curve A, CsCl (0.1 M) (2 cycles) (v=5 mV/s), curve B, BaCl₂ (0.1 M) (v=5 mV/s); (b) curve C, CoCl₂ (0.1 M) (v=25 mV/s): PPy/PSSO₃ reduction (1), Co²⁺ reduction in Co (m) (2), Co (m) stripping (3), PPy/PSSO₃ reoxidation (4).
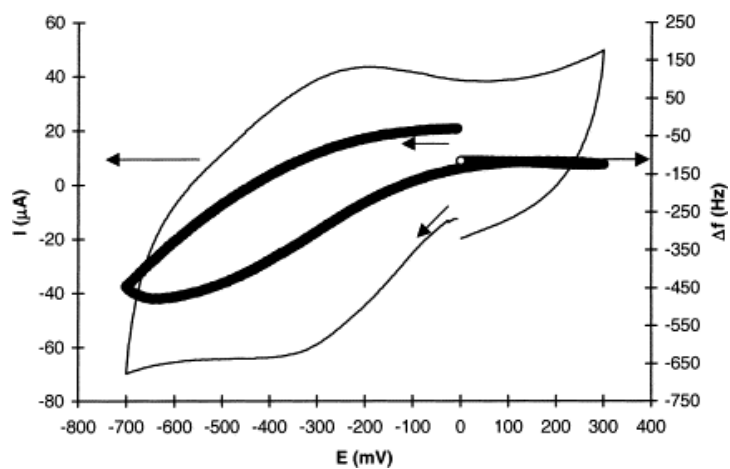

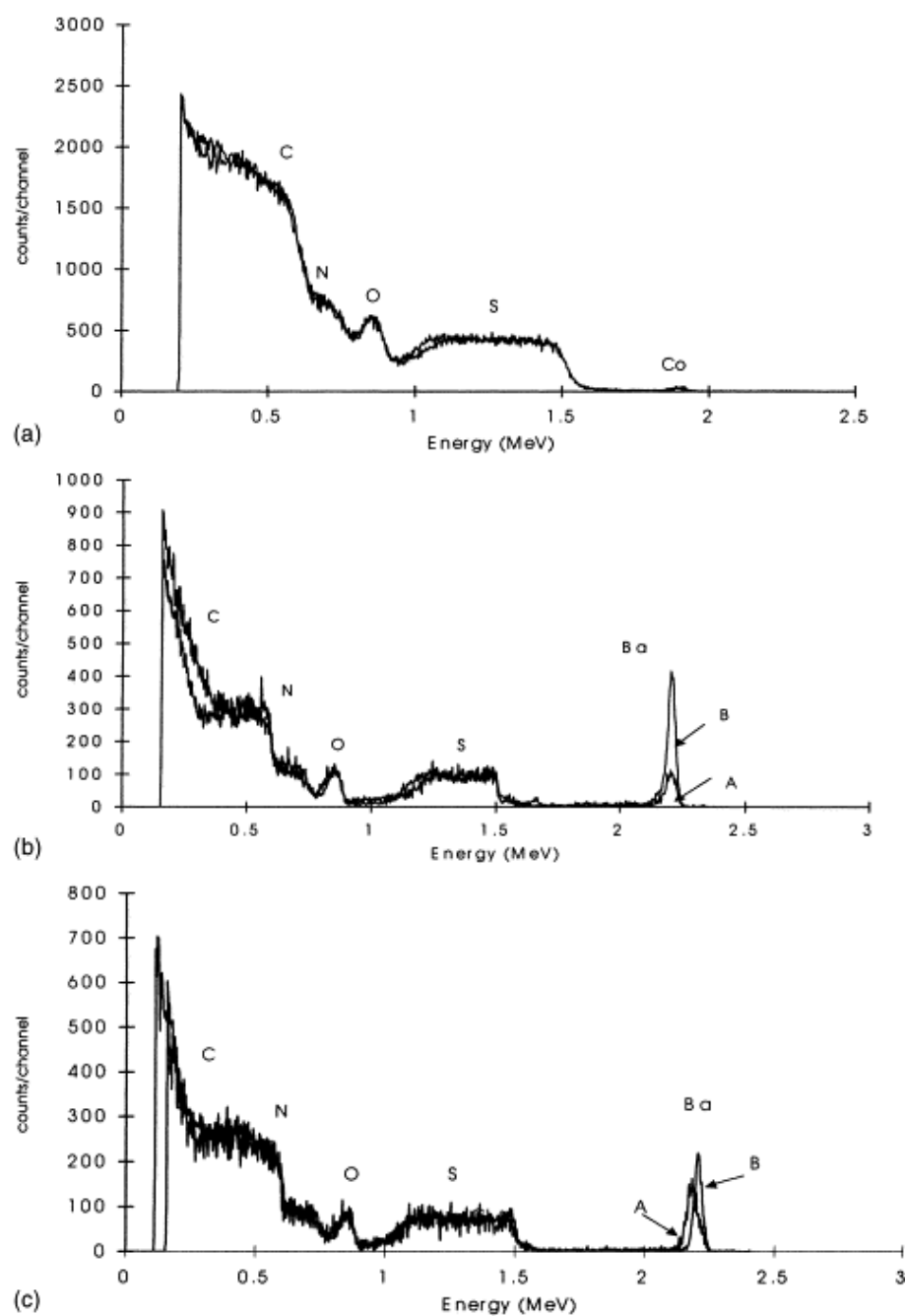Fig. 2. Potentiodynamic i/E and Δf/E profiles for PPy/PSSO₃ film in CoCl₂ (0. 1 M) aqueous solution.

Fig. 3. RBS spectra for PPy/PSSO$_3$ films deposited onto C and (a) reduced in CoCl$_2$ (0.1 M) aqueous solution, E$_r$=−0.7 V and E$_r$=−0.95 V; (b) reduced in BaCl$_2$ (0.1 M) aqueous solution: curve A, first fixation, curve B, tenth fixation; (c) reduced and reoxidized in BaCl$_2$ (0. 1 M) aqueous solution: curve A, first release, curve B, tenth release.

Table 1. SEM/EDAX quantification of the fixation and release of CsCl by the PPy/PSSO$_3$ resin

Sample	S (at.%)	Cs (at.%)	Cl (at.%)	Cs/S (at.%)
PPy/PSSO$_3$ Q_r=130 mC in CsCl 10^{-2} M	1.48	1.26	–	85
PPy/PSSO$_3$ Q_r=50 mC in CsCl 10^{-2} M	2.59	1.34	–	52
PPy/PSSO$_3$ Q_r=130 mC in CsCl 10^{-1} M	0.47	0.69	0.21	100
Ppy/PSSO$_3$ Q_r=Q_{ox}=130 mC in CsCl 10^{-1} M	1.28	0.36	0.35	0

PPy/PSSO$_3$ films (Q_s=1 C) have been reduced in 0.01 M CsCl aqueous solution, the fixation of Cs$^+$ being investigated by SEM/EDAX analysis (Table 1). The amount of fixed Cs$^+$ depends on the reduction of the polymer resin, since the Cs/S atomic ratio increases with the reduction current quantity. A reduction current of 130 mC results in the fixation of one Cs$^+$ cation by more than 85% of the sulfonate groups. However, when the current quantity is decreased by 2.6(130/50), the amount of fixed Cs$^+$ is decreased by only 1.65(1.93/1.17). This discrepancy may indicate that part of Cs$^+$ is merely fixed by static equilibrium between the film and the solution. In order to support this hypothesis, an oxidized PPy/PSSO$_3$ film has been equilibrated in KCl solution for 2 h, rinsed with water, dried and the S/K ratio has been measured by SEM/EDAX analysis. Since the PPy film is in the oxidized form and non polarized, K$^+$ cations could be exchanged for the proton of sulfonate groups inactive in the resin. According to the mechanism of the PPy synthesis, two protons are released per Py unit incorporated in the polymer, which may lead to marked local decrease of pH and thus to the protonation of inactive sulfonates [9]. Furthermore, K$^+$ could also be fixed by some active sulfonate sites which are liberated by partial reduction of the cationic PPy depending on the solution concentration [10]. The S/K atomic ratio is 1.7, which indicates quite an important binding of K$^+$. According to the scientific literature [10], the potential of a C/PPy/Cl electrode drops rapidly with time, then more slowly after 2 h for reaching a stable value after 50 h. Although, only few seconds are required for the electrochemical cation fixation, the static equilibrium can contribute to the incorporation of Cs$^+$ which is not monitored by coulometry.

When the PPy/PSSO$_3$ resin is reduced in more concentrated CsCl solution (10^{-1} M), it appears that CsCl is precipitated onto the film surface (Table 1). This salt precipitation is frequently observed when a metal is electrochemically deposited from organic solutions of chloride salts [11]. Fixation of Cs$^+$ as counter-ion of the polymer results in an excess of Cl$^-$ anions in the very close vicinity of the electrode leading to the insolubility and precipitation of CsCl on the electrode surface. Although, the solubility of these salts is much more limited in organic solvents than in water, this precipitation might also occur in concentrated aqueous solutions.

If each Cl$^-$ is supposed to be counter-ion of Cs$^+$, then 0.21 at.% of Cs is part of the precipitate, and the remaining 0.48 at.% are Cs$^+$ counter-ions of sulfonate groups, thus supporting that each sulfonate is associated to a Cs$^+$ cation and that all the sulfonate groups are accessible at least within 1 μm thickness.

After anodic polarization of the prereduced film in CsCl (Q_r=Q_{ox}), the precipitated CsCl salt is not redissolved (Table 1) but the total amount of fixed Cs$^+$ cation by sulfonate groups can be released showing the good reversibility of the Cs$^+$ exchange by the PPy/PSSO$_3$ resin. The Cs$^+$ cations which have been fixed by static equilibrium are also released, meaning that PPy chains are extensively reoxidized upon anodic polarization.

The binding of Ba^{2+} cations has been analyzed by the RBS technique. Fig. 3b is the RBS spectrum of the PPy/PSSO$_3$ film (Q_s=900 mC) reduced in Ba^{2+} solution (Q_r=6 mC). All the peaks characteristic of the elements of the polymer (C, N, O, and S) followed by peaks of Cl and Ba are observed upon increasing energy. Since similar spectrum was reported for the fixation of La^{3+} cations [2], some comparison will be made with Ba. The half-width of the S and Ba peaks agree with the superficial binding of Ba^{2+} cations as previously observed for La^{3+}. The cations are concentrated in a superficial layer of ca. 0.25 μm for Ba and 0.5 μm for La, beyond which their concentration linearly decreases. Lanthanum appears to penetrate more deeply the film than Ba, possibly as result of the lower charge density of Ba^{2+} (1.49e/Å) compared with La^{3+} (2.83e/Å), that would accordingly diffuse more slowly in the polarized film.

From the surface area of the characteristic peaks, the atomic S/Ba and S/La ratios have been calculated as 1/0.06 and 1/0.02, respectively. The small incorporation of these two cations compared with Cs$^+$ (S/Cs=1/0.8) is the consequence of the smaller reduction capability of the PPy/PSSO$_3$ film in multicharged-cation solutions. The current reduction quantity is only 6 mC in LaCl$_3$ and BaCl$_2$ solutions, thus much less than the 130 mC in the CsCl solution. That less La^{3+} is incorporated compared with Ba^{2+} could be at least partly explained by the difference in the cation charge, three sulfonate groups being required for the La^{3+} fixation instead of two for Ba^{2+}.

The observation of the Cl peak in the RBS spectrum indicates that BaCl$_2$ is also precipitated as CsCl in decimolar solution.

The RBS spectrum of the PPy/PSSO$_3$ films reduced and reoxidized in BaCl$_2$ allows to estimate the reversibility of the exchange of the Ba^{2+} cations (Fig. 3c). The Ba peak does not disappear upon reoxidation of the resin, indicating that the Ba release is incomplete. 50% of the fixed Ba is actually released. The Ba/Cl atomic ratio is 1 for the reoxidized film, which means that only part of the residual Ba originates from BaCl$_2$ on the film surface.

Similarly, 85% of the fixed La was released, and the La/Cl atomic ratio was 1/2 for the reoxidized film, so that part of residual La remains trapped in the film as counter-ion of the sulfonate functions. In contrast, the SEM/EDAX analysis of the reoxidized polymer film agrees with a Cs/Cl atomic ratio of 1 (Table 1) when the Cs^+ cation is concerned.

This observation is consistent with the reversible exchange of Cs^+, although the film surface is contaminated by the chloride salt during the release process. When the fixed cations are La^{3+} and Ba^{2+}, the same contamination occurs but the release process is less complete, some cations remaining counter-ion of sulfonate functions in the film. Limited reoxidation of the reduced PPy chains could account for this observation.

The RBS spectrum recorded after 10 binding/release cycles (Fig. 3b, curve B) for the film in the reduced state (corresponding to the Ba binding) shows that Ba remains accumulated in the superficial layer of the film (partly precipitated as $BaCl_2$) and has no significant tendency to penetrate more deeply in the film, since the width of the Ba peak remains essentially unchanged in contrast to what happened for La^{3+} cations. The more superficial binding of Ba and the slower diffusion in the film compared to La could explain this difference.

The RBS spectrum of the $PPy/PSSO_3$ film in the oxidized form after 10 Ba^{2+} binding/release cycles shows the accumulation of Ba at the polymer surface (Fig. 3c, curve B). Since in the case of La^{3+}, no cation accumulation was observed precipitation of $BaCl_2$ appears to be more important than that one of $LaCl_3$.

A limited reversibility of the PPy redox process could explain the loss of reversibility observed for multivalent cations. Some inactive sulfonate groups in the resin could be responsible for this loss of reversibility. If the ionic bonds that link multivalent cations to the resin are not broken simultaneously, the inactive sulfonate group can compensate the positive charge of the cation that remains irreversibly attached to the resin. Nevertheless, partial complexation of the cations by the PPy heterocycles could also play some role.

3.2. Polypyrrole/heptanesulfonate resin (PPy/HeptSO$_3$)

Since inactive sulfonate groups can contribute to the partial reversibility of the exchange of multicharged cations, a resin containing monosulfonate counter-ions has been synthesized. Since heptane sulfonate can only be incorporated in polypyrrole as active counter-ion of PPy, no inactive sulfonate can be made available in the resin.

The Cyclic voltammogram of $PPy/HeptSO_3$ in aqueous $LaCl_3$ solution (Fig. 4) shows two reduction waves at 0.1 and -0.4 V/SCE, respectively. Since anion expulsion is faster than cation incorporation [12], heptane sulfonate is partly expelled from the PPy resin during the first reduction wave, and La^{3+} cations are incorporated at more cathodic potential.
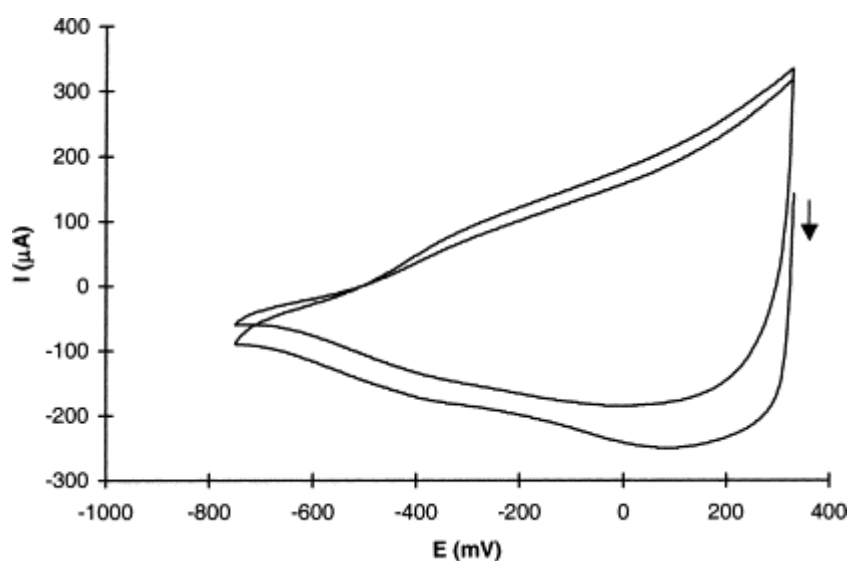

Fig. 4. Cyclic voltammogram (v=50 mV/s) for PPy/HeptSO₃ film in LaCl₃ (0. 1 M) aqueous solution (2 cycles).

RBS analysis of the PPy/HeptSO$_3$ film (Q_s=300 mC, Q_r=37 mC) reduced in LaCl$_3$ solution confirms that heptane sulfonate remains partly trapped in the PPy resin and contributes to La binding (Fig. 5a). Since the La/S atomic ratio is 0.02 for the reduced PPy/HeptSO$_3$ resin, the film is not totally reduced, some cationic PPy sites remaining associated to sulfonates. The same situation prevails in the PPy/PSSO$_3$ resin which limits the S/La ratio at 0.06. The cation fixation is however, more effective in case of the PPy/PSSO$_3$ resin, because of the possible contribution of the inactive sulfonate functions to the static binding of cations.
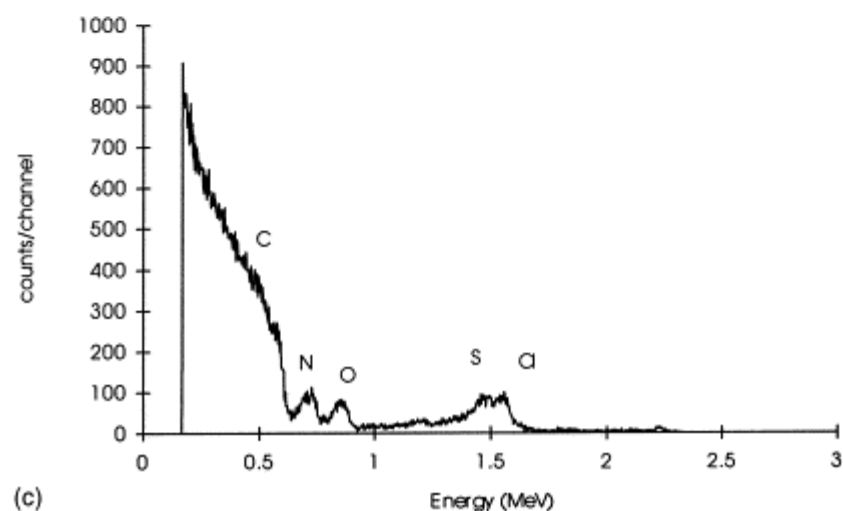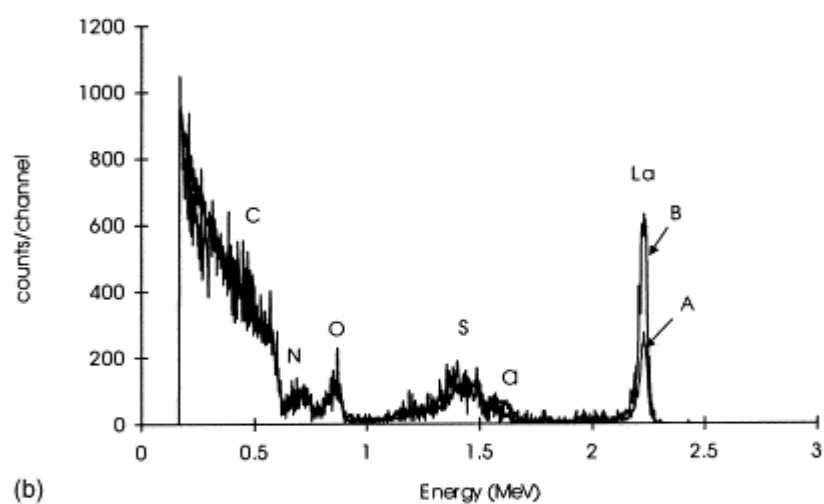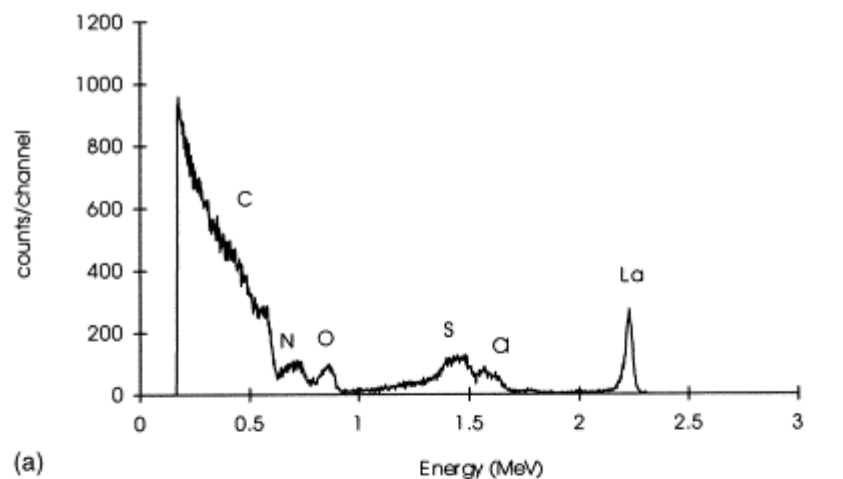
Fig. 5. RBS spectra (a) for PPy/HeptSO₃ film deposited onto C and reduced in LaCl₃ (0. 1 M) aqueous solution; (b) after reduction in LaCl₃ (0. 1 M) aqueous solution of: curve A, PPy/HeptSO₃ film, curve B, PPy/PSSO₃ film; (c) for PPy/HeptSO₃ film deposited onto C, reduced and reoxidized in LaCl₃ (0. 1 M) aqueous solution.

When the surface area of the RBS peak of La is compared for the PPy/HeptSO$_3$ and PPy/PSSO$_3$ films synthesized and reduced under the same conditions (Q_s=300 mC, Q_r=36 mC) (Fig. 5b), less La is fixed in case of PPy/HeptSO$_3$. Two major reasons can explain this difference. Firstly, the reduction current being the same for the two samples, less sulfonate sites are available for the cation fixation in the PPy/HeptSO$_3$ resin since some counter-ions are released during reduction. The smaller S peak of the reduced PPy/HeptSO$_3$ film compared to the PPy/PSSO$_3$ film is the consequence of the partial expulsion of the HeptSO$_3$ counter-ion. Secondly, part of the sulfonate groups in the PPy/PSSO$_3$ film are not counter-ions of PPy cationic sites and are available to La fixation by static exchange with H$^+$, so increasing the La fixation independently of the resin reduction. The PPy/HeptSO$_3$ is thus accordingly less effective in binding cations than PPy/PSSO$_3$.

The RBS spectrum of the reoxidized PPy/HeptSO$_3$ film shows that the reversibility is improved compared with the PPy/PSSO$_3$ resin (Fig. 5c). In the absence of inactive sulfonate groups, no La peak can be detected. An important amount of Cl is also observed (S/Cl=1), which indicates that half the sulfonate groups have been expelled during the reduction process and replaced by Cl anions during reoxidization.

The reversibility of the exchange of multivalent cations is improved when the monofunctional HeptSO$_3$ counter-ion is used instead of PSSO$_3$. Complexation of La by PPy chains should thus not be responsible for the limited reversibility of the PPy/PSSO$_3$ system as previously suggested, although the PPy chains packing might be different in relation to the polymeric structure of the counter-ion and possibly more favorable to complexation [13].

The efficiency of the cation fixation is however lower for PPy/HeptSO$_3$ because of the partial expulsion of the dopant. It could be improved by using longer alkyl chains since it has been reported that chains longer than C10 are irreversibly fixed in PPy [14].

3.3. Polypyrrole/styrenesulfonate resin (PPy/StySO₃)

A possible way to irreversibly insert a monofunctional anion in PPy could consist in using an unsaturated monoanionic counter-ion in the PPy synthesis followed by reaction of the unsaturation with the conducting polymer. In order to optimize the binding efficiency and the reversibility of the ion exchange, the synthesis and redox properties of polypyrrole doped by styrene sulfonate have been studied. Comparison with the PPy/PSSO$_3$ resin has been considered in order to clear up the actual role of the inactive sulfonates in the reversibility of the process.

Since the double bond of styrene sulfonate might be unstable under the anodic conditions required by the PPy synthesis, the stability of this salt has been checked in solution free from monomer by cyclic voltammetry coupled with the QCM analyzer. Only the solvent reaction is observed when the anodic potentials are scanned until +1.1 V, and no precipitation occurs on the electrode surface as confirmed by QCM. Although, counter-ion of the styrenic type is stable under anodic polarization, its polymerization might be initiated at high potentials (>1 V) by oxygen radicals formed as result of the solvent electrolysis and be undetected by QCM since the polymer (PSSO$_3$) is soluble in water.

In the presence of pyrrole, a polymerization peak is observed at 0.5 V/Pt leading to precipitation of polypyrrole on the anode as supported by a large decrease in the QCM frequency (increase in mass). Fig. 6 shows the dependence of the quartz frequency on the current quantity consumed by the pyrrole oxidation at constant potential of 0.7 V/Pt. Comparison of the PPy/StySO$_3$ and PPy/PSSO$_3$ systems shows that the initial mass increase (i.e. for current quantity <2 mC/0.2 cm^2) is smaller in case of PPy/StySO$_3$. For longer polarization times, the two curves are linear and nearly parallel, indicating quite comparable mass increase. Polypyrrole, and the counter-ions and solvation molecules it contains account for the mass increase probed by QCM. The mass of polypyrrole including the counter-ions formed by 5 mC current is 2.70×10^{-6} g calculated by the Faraday's law on the assumption that 2.3e are consumed per monomer unit [15]. The mass of the film deposited has also been calculated from the QCM data and the Sauerbrey equation as reported in Table 2. Expectedly, the experimental mass of the PPy/PSSO$_3$ film (QCM) is higher than the calculated one (coulometry), as result of inactive sulfonate groups formed in the initial stage of the polymerization. In case of PPy/StySO$_3$, the experimental mass is smaller than the predicted value, probably reflecting a doping level slightly lower than 0.3. Although, inactive

towards PSSO$_3$ and HeptSO$_3$, the radical cations that propagate the Py polymerization can react with styrene sulfonate resulting in shorter polypyrrole chains and thus in shorter conjugation length that limits the doping level.
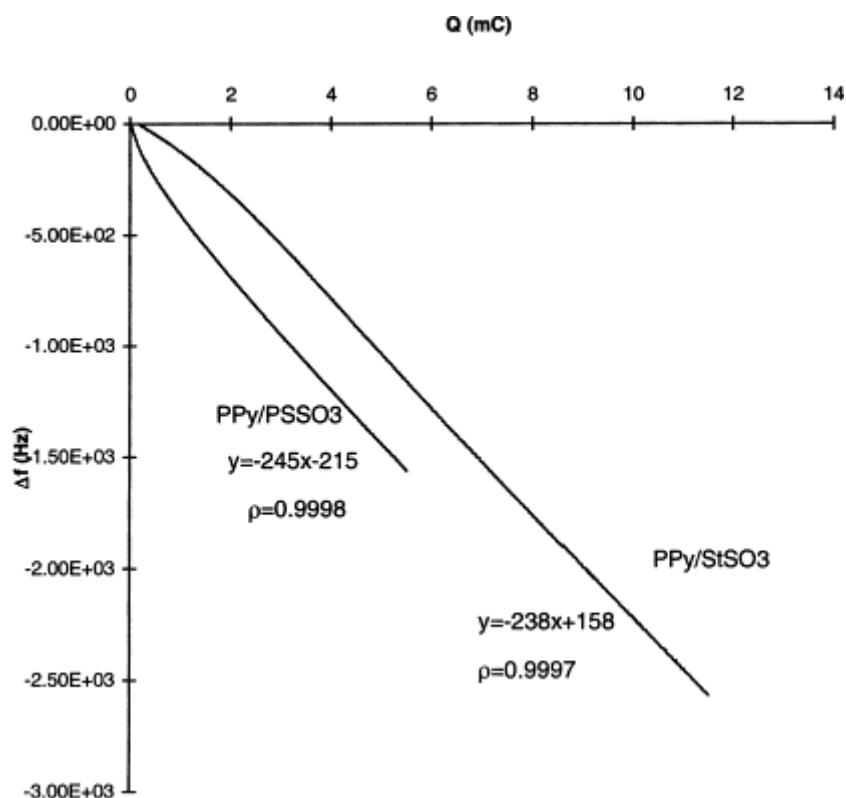

Fig. 6. Electrogravimetric quartz crystal microbalance profile vs. current quantity for the potentiostatic polarization (E=0.7 V) of aqueous solution of Py (0.1 M) and PSSO$_3$Na (0.1 M) or StySO$_3$Na (0.1 M).

Table 2. Comparison of the amount of PPy/PSSO$_3$ and PPy/StySO$_3$ deposited on Pt. Calculation by coulometry and measurement by QCM

PPy film	Q_s (mC)	m_{coul} (g)	m_{QCM} (g)
PPy/PSSO$_3$	5	2.70×10^{-6}	3.23×10^{-6}
PPy/StySO$_3$	5	2.70×10^{-6}	2.33×10^{-6}
PPy/StySO$_3$	10	5.40×10^{-6}	4.98×10^{-6}

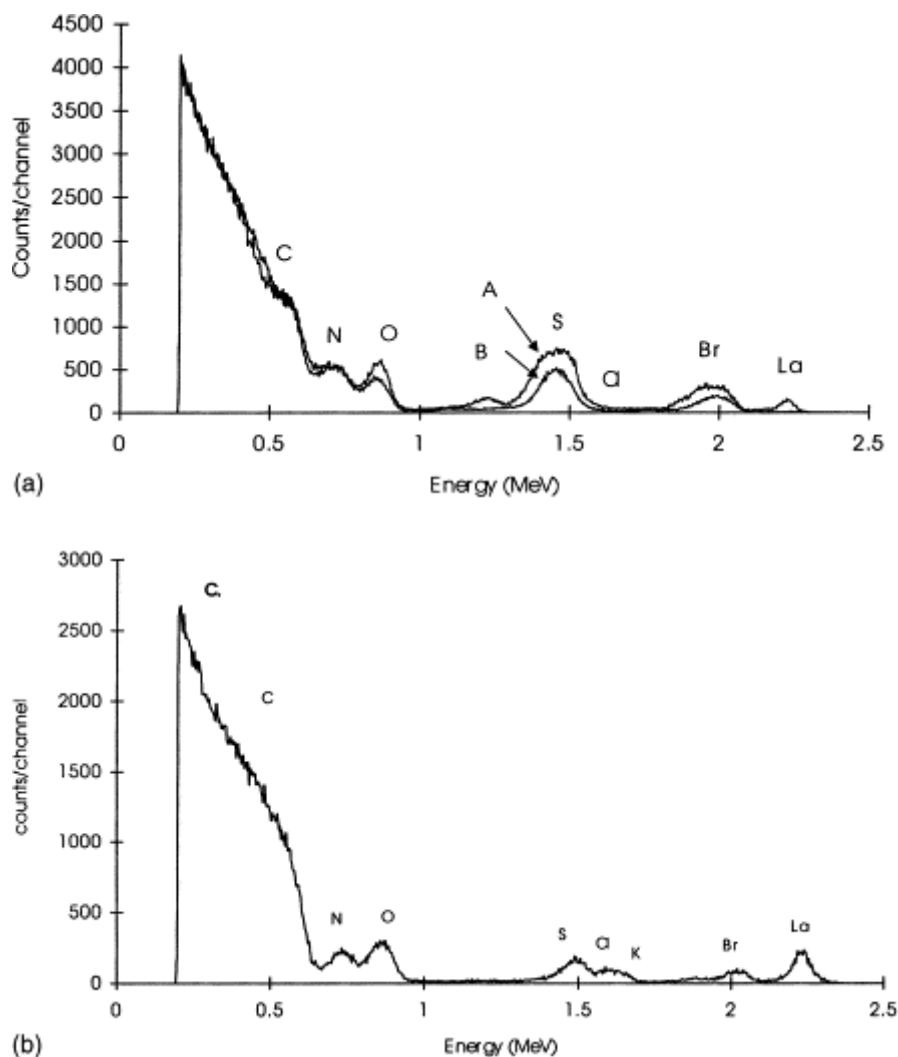*Fig. 7. RBS spectra for PPy/StySO₃ films deposited onto C: (a) curve A, after synthesis, curve B, after reduction in LaCl₃ (0.1 M); (b) curve C, after reduction in LaCl₃ (0.05 M)/KCl (0.05 M) aqueous solution.*

After washing with bidistilled water, the pristine PPy film has been analyzed by RBS (Fig. 7a, curve A). The spectrum confirms the incorporation of the StySO₃ counter-ion in agreement with a marked peak for S together with peaks for C, N and O. A large peak at 2 MeV is the signature of a contaminating element in the whole film thickness. Proton induced X-ray emission analysis (PIXE) [16] allows to assign this peak to bromide, whose the origin is still unclear.

The electroactivity of the PPy/StySO₃ film and the ion motion during the redox process have been studied. Cyclic voltammetry has been carried out in decimolar CsCl aqueous solution with the PPy/StySO₃ film deposited onto Pt (Fig. 8). A well-defined redox process is observed that corresponds to the PPy reduction at −0.6 V and reoxidation at −0.3 V. The PPy electroactivity is not perturbed by the unsaturated counter-ion. Simultaneously, the QCM shows a mass increase (frequency decrease) from 0 to −1 V, in line with the cation insertion rather than the expulsion of the StySO₃ anions. When the film is reduced, this observation is in contrast to the behavior of the PPy/toluene sulfonate resin that lost the major part of the anions upon reduction [17]. Assuming that volume and hydrophobicity of these two anions (*p*-toluene sulfonate and styrene sulfonate) are quite comparable, the difference observed might be accounted for by the reaction of the double bond of StySO₃ with growing PPy, so leading to the irreversible incorporation of these anions to the resin. Therefore, no post treatment of the film (e.g. UV irradiation or thermal treatment), is required for attaching permanently the counter-ions to the PPy matrix.
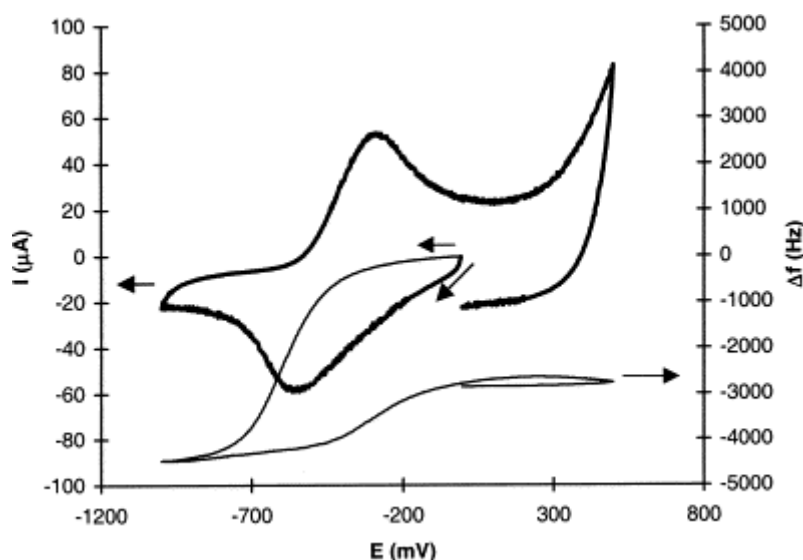
Fig. 8. Potentiodynamic i/E and Δf/E profiles for the PPy/StySO₃ film in CsCl (0.1 M) aqueous solution.

From the $\Delta f/E$ curve monitored during the film reoxidation (Fig. 8), cations are released as supported by QCM. However, although the redox process appears to be reversible ($Q_{red}=Q_{ox}$), the starting frequency is not restored which indicates that the process is partly irreversible. These observations are qualitatively reminiscent of the behavior of the PPy/PSSO₃ resin which is suitable to the fixation and release of cations.

The ion-exchange process has been further analyzed by the RBS technique. A PPy/StySO₃ film (Q_s=300 mC) has been reduced in decimolar LaCl₃ aqueous solution (Q_r=18 mC) (Fig. 7a, curve B). The RBS peak assigned to S remains detected for the reduced film, which confirms that at least part of the StySO₃ counter-ions remains trapped in the PPy matrix. However, comparison of Fig. 7a, curves A and B shows a decrease in the intensity of peaks for S and O compared to N, consistently with the partial release of StySO₃ during reduction. A decrease of the intensity of the peak assigned to Br is also clear, which suggests that this impurity is associated to the counter-ion rather than to the PPy chains.

The S/La atomic ratio (Q_r=18 mC) has been calculated (0.3) from the peak surface ratio, considering that the penetration thickness of La is 50 nm. The La fixation by PPy/StySO₃ (0.12 when Q_r=6 mC) is much more important than by PPy/PSSO₃ (0.06; Q_r=6 mC), although being much more superficial (penetration thickness in PPy/PSSO₃ was 100 nm). This difference might be explained by precipitation of La(StySO₃)₃ salt on the PPy/StySO₃ surface, this salt being insoluble in water, in agreement with the partial release of StySO₃ upon PPy/StySO₃ reduction. This phenomenon is inhibited in the PPy/PSSO₃ resin, leading to deeper La incorporation and to S/La ratio lower than 0.3.

Upon reoxidation of the PPy/StySO₃/La film, only a small part of La is released (S/La 0.2), the insoluble salt on the surface preventing the complete release of La. The RBS peak of Cl at 1.6 MeV is important which may suggest that Cl⁻ is substituted for StSO₃ that remains precipitated on the PPy surface.

These observations have heen confirmed by radiometric measurements of films reduced and reoxidized in ThCl₄ aqueous solution. A slightly higher activity is measured for reduced PPy/StySO₃ (Q_r=36 mC; Activity=382 counts/10000 s) than for the PPy/PSSO₃ film (Q_r=36 mC; ACTIVITY=305 counts/10000 s). Although, less marked than in case of La, PPy/StySO₃ appears to be more effective than PPy/PSSO₃ resin in binding Th. After reoxidation of the PPy/StySO₃ resin, the α activity (210 counts/10000 s) agrees with release of 45% Th.

The exchange reversibility is not improved when PPy/StySO₃ is compared with PPy/PSSO₃, since the La(StySO₃)₃ and Th(StySO₃)₄ salts are insoluble in water. During reoxidation, the precipitated salt remains on the PPy surface and the Cl anions penetrate the film from the solution in order to compensate the positive charge of the reoxidized PPy. In addition, during the oxidation, some film contraction can occur, which may prevent ion pairs from being washed from the resin [18].

3.4. Competitive binding of cations

The possible selectivity of the PPy/PSSO$_3$ resin in binding cations in mixture has been tested. Table 3 compares the α-activity measured for three PPy/PSSO$_3$ films reduced in pure Th(NO$_3$)$_4$ and in Th(NO$_3$)$_4$/NaNO$_3$ and Th(NO$_3$)$_4$/LaCl$_3$ mixtures. The α-activity is decreased when Na$^+$ competes with Th^{4+} in nitrate solution. The amount of Th fixed is decreased by 44%. Since the solution is equimolar in each salt and since only one sulfonate is needed to bind Na$^+$ compared to three sulfonates for the Th binding [2], there is some preference of the resin for Th.

Table 3. α-activity of PPy/PSSO$_3$ films reduced in salt solutions

Solution composition	Q_r (mC)	Activity (counts/10000 s)
Th(NO$_3$)$_4$ 0.1 M	87	1134
Th(NO$_3$)$_4$ 0.1 M NaNO$_3$ 0.1 M	87	749
Th(NO$_3$) 0.1 M/LaCl$_3$ 0.1 M	87	2808

The reverse trend is observed when Th(NO$_3$)$_4$ is mixed with LaCl$_3$. An important increase of the α-activity is observed as result of the film reduction, which is explained by the precipitation of ThCl$_4$ on the film surface. This precipitation which did not take place in pure Th(NO$_3$)$_4$ solution, is restored in the presence of the chloride anions inserted with the lanthanum cations.

Finally, the two cations are inserted when a PPy/StySO$_3$ film is reduced in the LaCl$_3$/KCl mixture. The RBS peaks characteristic of La and K are observed in Fig. 7b, curve C. However, the partial superposition of the K and the Cl peaks does not allow selectivity to be analyzed further.

4. Conclusion

Compared to the PPy/HeptSO$_3$ and PPy/StySO$_3$ combinations, the PPy/PSSO$_3$ resin is most appropriate to the binding of various cations, since the sulfonate counter-ion is then irreversibly incorporated in the PPy matrix. The reversibility of the ion exchange is complete for monovalent cations, which is no longer the case when multicharged cations are considered.

The reversibility is improved when the monovalent HeptSO$_3$ is used as counter-ion, which indicates that complexation of multivalent cations by the PPy backbone is not at the origin of the lower reversibility exhibited by the PPy/PSSO$_3$ resin. The progressive loss of the HeptSO$_3$ counter-ion in favor of Cl$^-$ switches the original cation exchange resin into an anion exchange one. The efficiency of cation binding thus remains better in case of the PPy/PSSO$_3$ resin.

The use of StySO$_3$ as counter-ion allows an electroactive polypyrrole film to be synthesized. Upon PPy reduction, monovalent cations are incorporated, whereas the important fixation of multivalent cation more likely results from the precipitation of the insoluble salt on the surface during reduction, leading to less reversible process.

When two cations compete for binding to the resin, the salt anion play an important role. Precipitation of metal chloride simultaneously to the polymer reduction can be avoided if nitrate is used instead of chloride. Since the reported results are essentially qualitative, it may only be concluded that the two cations originally in solution are bonded to the resin.

Acknowledgements

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