Electrochemical Study of the Uranium Exchange by Polypyrrole-Based Resins

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ABSTRACT: Electrochemical control of the binding of uranium ions by redox active polypyrrole resins was studied. The experimental conditions for this binding were optimized with respect to the uranium ions to be fixed, the resin, and the solution. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 3473–3484, 1999

Key words: waste treatment; electrochemical process; radioactive ions; conducting polypyrrole

INTRODUCTION

Increasing attention is being paid nowadays to the treatment of low-activity radioactive wastes by organic polymers.[1–5] Two main strategies have been proposed for this purpose.

The first approach requires the availability of complexing polymers able to fix selectively the contaminating ions.[1–3] This technique has been carried out elsewhere for the binding of uranium by polyvinylimidazole (PVI).[4] The last step of the process could be the burning of the metal/polymer complex with recovery of the metal.

The second strategy that we are going to explore consists of a reversible process based on the fixation or release of ions by the application of a specific potential.[5] The large development of electroactive polymers,[6] and, particularly, electronically conducting polymers, makes this potentio-controlled process a very promising technique. Ions can indeed be exchanged between the solution and the polymer when the polymer is reduced and reoxidized (Scheme 1).

Depending on the size of the anions incorporated into the conducting polymer, two types of resins are available. If the anions are of small size, they can be exchanged and the resin is anionic [Scheme 1(A)]. In the case of polymeric anions, such as poly(styrene sulfonate) ($PSSO_3$), the entanglement of the polypyrrole (PPy) and $PSSO_3$ chains prevents anions from being released. As a result, cations are exchanged during the electrochemical redox process [Scheme 1(B)].

PPy is a good candidate for this type of resin since it is stable, electroactive, and insoluble in aqueous media. Moreover, it can be electrochemically synthesized in aqueous solution, and its ability to fix and to release anions (Cl^-, ClO_4^-, . . .)[7] and cations (Th^{4+}, La^{3+}, Cs^+, Ba^{2+}, . . .)[8,9] has already been reported. Since the cations are not reduced to the metallic state in water and no intermediate oxidation state (i.e., Th^{3+}, La^{2+}, or Ba^+) is known, only electrostatic interaction between these cations and the polarized PPy resin can occur. This behavior is, however, different in the case of UO_2^{2+} and U^{4+} cations, which show an intermediate oxidation state. UO_2^{2+} can, however, be electrochemically reduced
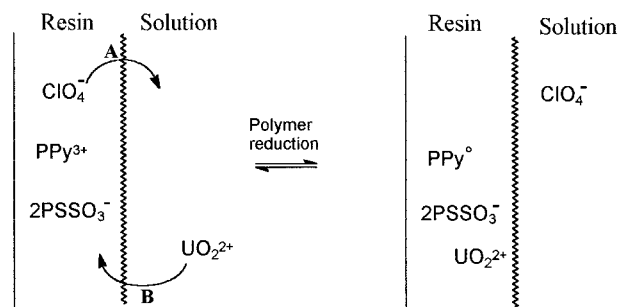
Scheme 1

to UO_2 (s) in water under well-defined experimental conditions.[10]

The aim of this article was to analyze the ability of both anionic and cationic PPy resins to fix uranium ions from various aqueous solutions. Uranium is actually used as a model for less electrochemically stable ions.

EXPERIMENTAL

$UO_2(NO_3)_2 \cdot 6H_2O$ was delivered by Fluka (Brussels, Belgium). Cs_2UCl_6 and UCl_4 were synthesized according to classical procedures and their structure and purity were confirmed by X-ray diffraction analysis. Bidistilled water was purged with nitrogen. Pyrrole (Aldrich, Steinheim, Germany) was freshly distilled under reduced pressure before use. Imidazole (Aldrich), $PSSO_3Na$ (Aldrich MW 70,000), and $LiClO_4$ (Aldrich) were used as received. PVI (M_v 30,000) was prepared by radical polymerization of vinylimidazole (Aldrich) initiated by AIBN (Acros, Geel, Belgium) in ethanol at 70°C for 12 h (see ref. 5 for more information).

Electrochemical polymerization and cyclic voltammetry were carried out using an EG&G Princeton Applied Research Model 263A potentiostat/galvanostat. All the experiments were performed under a nitrogen atmosphere in a closed cell, using platinum (1 cm^2) or glassy carbon (1.5 cm^2) as a working electrode and a platinum sheet as a counterelectrode. A platinum sheet was also used as a pseudoreference.

The electrochemical synthesis of PPy was achieved under potentiostatic conditions (Es = 0.7 V/SCE) in aqueous solutions of pyrrole (0.1M) and $LiClO_4$ (0.1M) or $PSSO_3Na$ (0.1M). Alpha counting was carried out with a VEMI counter working at 1400 mV for 10,000 s.

RESULTS AND DISCUSSION

Before the systematic study, preliminary experiments were performed. First, the electroactivity window was determined for each solution [i.e., Cs_2UCl_6, UCl_4, and $UO_2(NO_3)_2$] as well as the redox activity of PPy in these solutions. It is essential to know the amount of uranium spontaneously adsorbed by the resin independently of any polarization. This amount was estimated from the α-activity of a PPy film that has been dipped in the uranium salt solution, carefully rinsed with water, and dried. This contribution is then subtracted from the α-activity measured for PPy resins that have been polarized in the same uranium solution. As a rule, PPy films are reduced (or oxidized) in the aqueous solution of the ion to be fixed, and the α-activity is measured after careful washing with water (or with HCl in case of fixation of the complex UCl_6^{2-}) and drying. Conversely, these reduced (or oxidized) films are oxidized (or reduced) in the same aqueous solution in order to evaluate the effect of the potential on the release of the bound ions.

Cs_2UCl_6 Solution

Cs_2UCl_6, which is commonly used in electrochemical research, was studied first. Since the predominant ionic radioactive species is U^{4+} in HCl 1M and UCl_6^{2-} in HCl 6M,[11] radioactive cations or anions are made available, so that the two types of PPy resins could be studied by using solutions of the same salt but at different pH.

Anionic Resin

In a 0.1M Cs_2UCl_6 aqueous solution, the electroactivity window extends from -0.25 to $+0.15$ V on Pt, the cathodic limit being dictated by the reduction of protons, and the anodic limit, by the oxidation of U (IV) in U (VI). Since the redox activity of the PPy/ClO_4^- film was observed in this solution [Fig. 1(A)], the effect of pH on the uranium binding and release can be studied according to the procedure shown in Scheme 2.

After synthesis, the PPy/ClO_4^- polymer is reduced in order to expel the ClO_4^- anions. After careful washing with bidistilled water under a nitrogen atmosphere, the reduced film is oxidized in the Cs_2UCl_6 solution in order to incorporate anions (Cl^- or UCl_6^{2-}). The fixed anions are released on subsequent reduction of PPy$^+$.

The anion fixation was studied from Cs_2UCl_6 solutions containing HCl in various concentra-
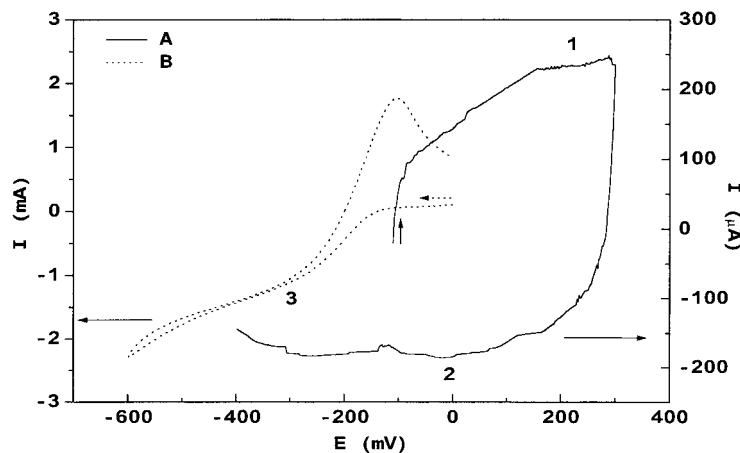
Figure 1 Cyclic voltammogram in $0.1M$ Cs_2UCl_6 aqueous solution: (A) on a prereduced PPy/ClO_4^- film deposited onto Pt (scanning rate: 50 mV/s); (B) on a $PPy/PSSO_3$ film deposited onto Pt (scanning rate: 20 mV/s); (1) PPy oxidation; (2) PPy reduction; (3) simultaneous reduction of $PPy/PSSO_3$ and H^+.

tions (no HCl, HCl $1M,$ and HCl $2M$). Table I shows that the oxidized polymer behaves quite similarly to the unpolarized PPy in the absence of HCl. The positively charged polymer has thus no particular affinity for the U^{4+} ions. A complete redox cycle does not change the situation, indicating that, in spite of its occurrence, a change in the resin morphology during the redox process cannot trap radioactive ions. When the HCl concentration is increased to $2M,$ the α-activity remains very low.

The electroactivity of PPy/ClO_4^- films in the Cs_2UCl_6 solution at high pH (HCl $6M$) disappears completely. The reduction and oxidation peaks of the PPy are indeed no longer observed by cyclic voltammetry in this very acidic solution. This loss of electroactivity has prevented this resin from being tested for fixation of the UCl_6^{2-} complex.

Cationic Resin

The PPy resin is now doped by poly(styrene sulfonate), that is, by a large size anion, and cations

are fixed under cathodic polarization (Scheme 3). Cyclic voltammetry on the $Pt/PPy/PSSO_3$ electrode in a Cs_2UCl_6 solution shows a wave starting at -0.15 V that could correspond to the PPy reduction and the simultaneous reduction of protons [Fig. 1(B)]. However, the electrochromism of the film (which is black in the oxidized form and becomes yellow in the reduced state) is not observed, making the actual reduction of the film questionable. Therefore, fixation of uranium has to be confirmed by radioactivity measurements.

Table II shows that no uranium is fixed as result of electrolysis for 2 min at -0.6 V, so that the polymer reduction cannot be ascertained. The small increase in α-activity when the PPy film is reduced at -1 V could result from precipitation of uranium hydroxide caused by the proton reduction and concomitant change in pH. These uranium hydroxides are not removed by washing with water (pH $>$ 4). Moreover, when the same electrolysis is carried out onto bare platinum, not only is the α-activity greater compared to the
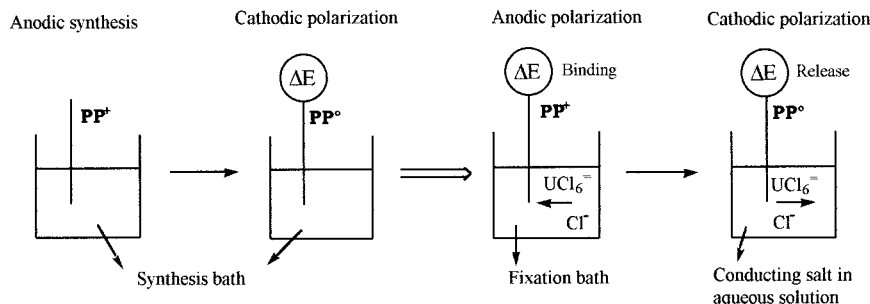
Scheme 2

Table I   α-Activity for Various PPy/ClO$_4$ Resins in Relation to the Electrochemical Treatment and pH of the Cs$_2$UCl$_6$ Solution

Electrode	Fixation Bath	Electrochemical Treatment	Activity (Counts/10,000 s)
PPy/ClO$_4$	Cs$_2$UCl$_6$	No polarization	4
PPy/ClO$_4$	Cs$_2$UCl$_6$	Oxidation 1 min at +0.1 V	19
PPy/ClO$_4$	Cs$_2$UCl$_6$	Oxidation then reduction	15
PPy/ClO$_4$	Cs$_2$UCl$_6$/HCl 1M	No polarization	5
PPy/ClO$_4$	Cs$_2$UCl$_6$/HCl 1M	Oxidation 1 min at +0.1 V	17
PPy/ClO$_4$	Cs$_2$UCl$_6$/HCl 1M	Oxidation then reduction	13
PPy/ClO$_4$	Cs$_2$UCl$_6$/HCl 2M	No polarization	14
PPy/ClO$_4$	Cs$_2$UCl$_6$/HCl 2M	Oxidation 30 s at +0.28 V	21
PPy/ClO$_4$	Cs$_2$UCl$_6$/HCl 2M	Oxidation then reduction	6

Pt/PPy/PSSO$_3$ electrode, but so are the amount of current and the proton reduction. This observation supports that the α-activity originates from precipitation of uranium hydroxide rather than from PPy reduction.

The same experiment was repeated with PPy/PSSO$_3$ deposited onto glassy carbon rather than onto Pt. The proton reduction is then shifted to more cathodic potential, which is suitable for the polymer reduction. However, the uranium binding is not improved. The low experimental α-activity could also be explained by competition between U^{4+} and Cs$^+$, for fixation, although the charge density is in favor of uranium. To avoid this competition, an aqueous solution of UCl$_4$ was studied.
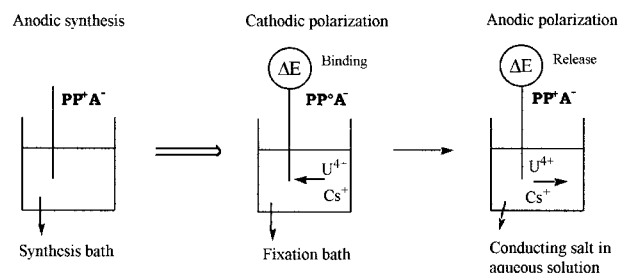
UCl$_4$ Solution

The α-activity measured for the PPy/PSSO$_3$ films reduced in a 0.1M UCl$_4$ solution (pH 1) shows that the uranium is not bound to the resin, although no cation is available to compete with uranium in this experiment. However, the UCl$_4$ solution is very acid and PPy is known to be protonated at low pH (<2) with formation of polycationic chains.[12] The film is no longer reduced and the positive charges of the polycation have to be compensated by anions that can be either PSSO$_3$ sites or small anions from the solution. Then, the resin behaves as an anionic resin and cannot bind the U^{4+} cations.

From the study of Cs$_2$UCl$_6$ and UCl$_4$ solutions, it appears that the fixation of the UCl$_6^{2-}$ complex by PPy/ClO$_4^-$ and that of U^{4+} by PPy/PSSO$_3$ are not effective since the pH is too low and prevents the polymer from being reduced. Then, the PPy/ClO$_4^-$ resin cannot fix UCl$_6^{2-}$, whereas the protonated PPy of the PPy/PSSO$_3$ resin consumes the sulfonate binding sites at the expense of the cation fixation. Although the cationic binding by the PPy/PSSO$_3$ resin in the Cs$_2$UCl$_6$ solution at higher pH (1M HCl) is possible, the unfavorable effect of the competition between Cs$^+$ and U^{4+} on the uranium binding has to be considered.

In some cases, the noxious effect of pH could be alleviated by the addition of a buffer. However, the additional salt will be at the origin of competition for the fixation of uranium (containing) anion or cation depending on the resin. For all these reasons, we have used the PPy/PSSO$_3$ resin in combination with solution of UO$_2$(NO$_3$)$_2$ which is less acidic [pH 2.5 for 0.1M UO$_2$(NO$_3$)$_2$] and does not contaminate the system by competing cations.

Anodic synthesis   Cathodic polarization   Anodic polarization

ΔE Binding   ΔE Release

PP$^+$A$^-$ PP$^\circ$A$^-$ PP$^+$A$^-$

Synthesis bath   Fixation bath   Conducting salt in aqueous solution

U^{4+} U^{4+}
Cs$^+$ Cs$^+$

Scheme 3

UO$_2$(NO$_3$)$_2$ Solution

Dynamic Fixation

Fixation of the uranyl cation requires the use of the cationic PPy/PSSO$_3$ resin according to Scheme 3. The cyclic voltammogram of a 0.1M aqueous solution of UO$_2$(NO$_3$)$_2$ shows two reduction waves at -0.45 and -1.350 V/Pt onto neat platinum. An oxidation peak is observed during the reverse scan at $+1$ V. When the scanning is

Table II α-Activity for Various PPy/PSSO₃ Resins in Relation to the Electrochemical Treatment and
of the Electrode Used

Electrode	Fixation Bath	Electrochemical Treatment	Activity (Counts/10,000 s)
Pt/PPy/PSSO₃	Cs₂UCl₆	No polarization	14
Pt/PPy/PSSO₃	Cs₂UCl₆	Reduction 2 min at −0.6 V	19
Pt/PPy/PSSO₃	Cs₂UCl₆	Prereduction in a separated bath	22
Pt/PPy/PSSO₃	Cs₂UCl₆	Reduction at −1 V	47
Pt	Cs₂UCl₆	Polarization 30 s at −0.55 V	59
C/PPy/PSSO₃	Cs₂UCl₆	No polarization	31
C/PPy/PSSO₃	Cs₂UCl₆	Reduction 30 s at −0.7 V	46
C/PPy/PSSO₃	Cs₂UCl₆	Reduction 1 min at −0.7 V	60
C/PPy/PSSO₃	Cs₂UCl₆	Reduction 2 min at −0.7 V	67
C/PPy/PSSO₃	Cs₂UCl₆	Reduction and reoxidized	47
C	Cs₂UCl₆	Polarization 1 min at −0.7 V	90

reversed after the first cathodic peak ($E = -1$ V), the anodic curve shows two peaks at $+0.1$ and $+0.3$ V. Moreover, the plot of the intensity of the first reduction peak versus the square root of the scan rate is linear and goes through the origin. This peak has thus been attributed to the reversible faradic reaction

$$UO_2^{2+} + e^- \rightleftharpoons UO_2^+$$
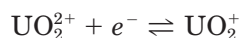
The second reduction was attributed to the irreversible reaction of uranium dioxide formation.

The first reduction of the divalent uranyl cation into a monovalent one is not troublesome for the uranium fixation by the PPy/PSSO₃ resin. The second reduction with formation of the insoluble neutral UO_2 (s) might be a problem, since the UO_2 (s) precipitation will erroneously increase the α-counting. This problem will, however, be avoided if the polymer reduction is less cathodic than is the uranyl one. The redox behavior of the PPy/PSSO₃ resin has thus been investigated in the same $UO_2(NO_3)_2$ solution (Fig. 2). A first reduction peak is observed at -0.6 V, whose intensity depends on the film thickness. The reduction of the polymer at this potential is confirmed by the change in color of the film (from black to yellow). Nevertheless, the intensity of this reduction wave is too high for being accounted for only by the polymer reduction. The reduction of the uranyl cations and the polymer are thought to occur simultaneously. The observation of a second reduction wave below -1 V is the signature for the reduction of UO_2^{2+} into insoluble uranium dioxide. The main conclusion is thus that the electroactivity of the conducting polymer is restored

in the $UO_2(NO_3)_2$ solution at pH 2.5, so that the uranium fixation is feasible at least in a potential range in which the complete reduction of the uranium cations is not observed.

The α-counting reported in Table III shows that reduction at -0.6 and -0.8 V does not provide very high activities, thus indicating a very limited fixation of uranium. The major part of the current should thus contribute to the uranium reduction rather than to the polymer reduction. A potential more cathodic than -0.8 V may not be used, since reduction of UO_2^{2+} and precipitation of UO_2 (s) already occur at this potential as ascertained by the α-activity of neat platinum used as electrode in parallel experiments. When this Pt electrode is polarized at $+0.125$ V, the α-activity completely disappears. The same observation was
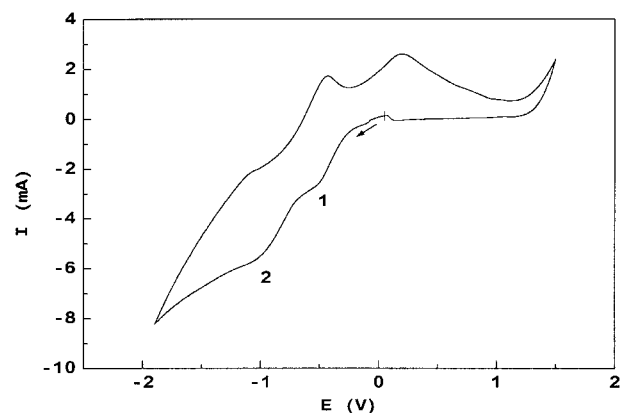

Figure 2 Cyclic voltammogram in 0.1M $UO_2(NO_3)_2$ aqueous solution on a PPy/PSSO₃ film deposited onto Pt (scanning rate: 5 mV/s): (1) reduction of UO_2^{2+} in UO_2^+; (2) reduction of UO_2^+ in UO_2 (s).

Table III α-Activity for Various PPy/PSSO$_3$ Resins in Relation to the Electrochemical Treatment

Electrode	Fixation Bath	Electrochemical Treatment	Activity (Counts/10,000 s)
Pt/PPy/PSSO$_3$	UO$_2$(NO$_3$)$_2$	Reduction 3 min at -0.6 V	41
Pt/PPy/PSSO$_3$	UO$_2$(NO$_3$)$_2$	Reduction 3 min at -0.8 V	60
Pt/PPy/PSSO$_3$	UO$_2$(NO$_3$)$_2$	Reduction 3 min at -1 V	268
Pt	UO$_2$(NO$_3$)$_2$	Polarization 3 min at -0.8 V	73
Pt/PPy/PSSO$_3$	UO$_2$(NO$_3$)$_2$	Reduction 3 min at -0.6 V and reoxidation 3 min at $+0.1$ V	13
Pt/PPy/PSSO$_3$	UO$_2$(NO$_3$)$_2$	No polarization	8
Pt/PPy/PSSO$_3$	UO$_2$(NO$_3$)$_2$	Washing during 5 min after reduction	141
Pt/PPy/PSSO$_3$	UO$_2$(NO$_3$)$_2$	Washing during 24 h after reduction	14
Pt/PPy/PSSO$_3$	UO$_2$(NO$_3$)$_2$	Oxidation 3 min at $+0.125$ V	15
Pt	UO$_2$(NO$_3$)$_2$	Polarization 3 min at $+0.125$ V	8

reported for the prereduced PPy/PSSO$_3$ film when polarized at $+0.1$ V. To make the polymer reduction more favorable, thicker films were synthesized. According to the scientific literature,[13] films thicker than 4 μm completely isolate the electrode surface from the solution, whereas the redox potential of thinner films exhibits a mixed potential of the two components: platinum and PPy. The setting of electrolysis time for the polymer synthesis is an easy way to control the thickness, which linearly depends on the current consumption (1 C/cm^2 leads to a 4 μm film[13]). Films of 2.6, 5.3, and 10.6 μm were synthesized.

The cyclic voltammograms of these three films in the 0.1M UO$_2$(NO$_3$)$_2$ solution are very similar. Only one reduction peak is observed at -0.9 V. Moreover, when the scanning rate is low (5 mV/s), the polymer reduction is more favorable and a well-defined reduction peak is observed followed by a clear decrease of the current intensity as result of the electrode passivation. Thus, the formation of the polymer and the complete reduction of UO$_2^{2+}$ into UO$_2$ (s) occur at well-separated potentials, so that the electrochemical process of interest can be properly controlled.

The experimental α-activity is more important compared to thin films (Table IV), although still low compared to the film capacity. Indeed, the fixation amounts to about 4% of the polymer capacity. The film reduction remains in competition with the first reduction of UO$_2^{2+}$ in UO$_2^{+}$.

Static Fixation

To completely avoid any interference between the uranyl reduction and the uranium fixation, the polymer was reduced before being dipped in the uranyl nitrate solution (see Scheme 4) under a nitrogen atmosphere. The electrochemical bath used for the PPy reduction contains a conducting salt with a monovalent cation which is electrochemically stable. This cation is inserted into the reduced PPy/PSSO$_3$ film and then exchanged with UO$_2^{2+}$ when the film is equilibrated in the UO$_2$(NO$_3$)$_2$ solution, the charge effect and the concentration being in favor of the incorporation of the divalent uranyl cations. The amount of uranium extracted by various samples is reported in Table V in relation to different experimental parameters.

Table IV α-Activity for PPy/PSSO$_3$ Resins of Various Thicknesses

Film Thickness (μm)	Fixation Bath	Electrochemical Treatment	Activity (Counts/10,000 s)
2.6	UO$_2$(NO$_3$)$_2$	Reduction 5 min at -0.9 V	345
5.3	UO$_2$(NO$_3$)$_2$	Reduction 5 min at -0.9 V	253
10.6	UO$_2$(NO$_3$)$_2$	Reduction 5 min at -0.9 V	361

Anodic synthesis   Cathodic polarization   Exchange equilibrium
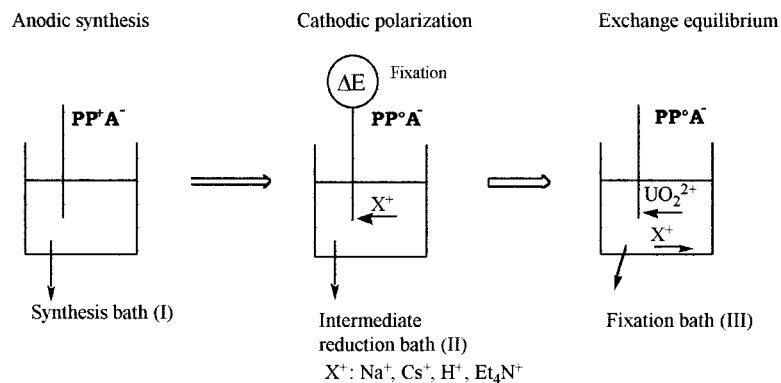
Scheme 4

Effect of the Equilibration Time. The PPy/PSSO$_3$ film was prereduced in a PSSO$_3$Na solution and the effect of the equilibration time on the uranyl fixation was investigated. The uranium content of the film increases when the equilibration time increases from 5 to 15 min. However, when PPy is allowed to equilibrate for 50 min, the experimental α-activity decreases. This detrimental effect can be explained by the low stability of the neutral PPy in the presence of oxidizing cations, such as UO$_2^{2+}$. Consistently, we have observed that the potential of the open circuit with the reduced PPy/PSSO$_3$ film increases with respect to calomel reference after dipping for 15 min in a UO$_2$(NO$_3$)$_2$ solution. In contrast, the potential remains essentially stable when NaCl is substituted for UO$_2$(NO$_3$)$_2$. The equilibration time has thus been fixed at 15 min for the forthcoming experiments.

Effect of the Nature of the Exchanged Ion. The nature of the conducting salt in the electrochemical bath used for the PPy reduction was also changed. Decimolar aqueous solutions each of NaCl, CsCl, HCl, and Et$_4$NCl were compared (bath II in Scheme 4) in order to know whether the cation to be exchanged for UO$_2^{2+}$ is of critical importance.

Although proton is *a priori* an interesting counterion due to the high strength of sulfonic acid, the electroactivity of the PPy/PSSO$_3$ resin in an acidic solution is rapidly lost (cf. *supra*). In agreement with the inhibition of the PPy reduction, a very small amount of uranium is fixed (Table V).

When UO$_2^{2+}$ is exchanged for Cs$^+$, no significant difference is observed with respect to Na$^+$, indicating that the charge density of the exchanged ion is of secondary importance. Finally, a lower α-activity is measured in the case of the organic Et$_4$N$^+$ cations, more likely because of a specific affinity for the organic matrix (Table V).

Effect of the Capacity. The effect of the resin capacity was investigated according to two experimental approaches. The number of sulfonate sites available to the uranium fixation was modified by changing the current quantity used to reduce the PPy/PSSO$_3$ film (Table V). There is a direct, although nonlinear, dependence between the current quantity and the α-activity.

The use of mixed PPy/PSSO$_3$/ClO$_4^-$ film, thus containing a mixture of small- and large-size anions, is another way to control the resin capacity. Indeed, the ClO$_4^-$ anions are extracted during the reduction step, so resulting in a resin of a lower capacity than that of the pure PPy/PSSO$_3$ resin. When the PSSO$_3^-$/ClO$_4^-$ molar ratio is 1/5, the uranium fixation is about 1/5 of the α-activity observed for the pure PPy/PSSO$_3$ resin (Table V). This observation is in favor of the UO$_2^{2+}$ binding by the sulfonate sites made available by the PPy reduction.

It must be noted that the use of mixed PPy/PSSO$_3$/ClO$_4^-$ films does not only lead to change in the resin capacity but also modifies the morphology and the hydrophilicity of the film,[14] the PPy/PSSO$_3$/ClO$_4^-$ (1/5) film being more granular and more hydrophilic than is the pure PPy/PSSO$_3$ film. Modification of these two parameters appears, however, to have a limited influence on the uranyl incorporation since about 1/5 of the α-activity is fixed on the PPy/PSSO$_3$/ClO$_4^-$ (1/5) film. A greater effect of these parameters was observed in case of the Th^{4+} fixation.[14] However, the reduction process was carried out *in situ* when Th^{4+} was concerned (Scheme 3), contrary to the static fixation process (Scheme 4) used to incorporate the uranyl cation.

Effect of the Ion Pair. Since the affinity of UO$_2^{2+}$ for carboxylate anions is greater than for sulfonate anions,[10] the PPy resin was doped with poly-

Table V α-**Activity for Prereduced PPy/PSSO$_3$ Resins, Equilibrated in Uranyl Nitrate Solution**

Resin	Electrochemical Treatment	t (min)	Activity (Counts/10,000 s)
PPy/PSSO$_3$	Equilibration after 50 mC reduction in PSSO$_3$Na	5	57
PPy/PSSO$_3$	Equilibration after 50 mC reduction in PSSO$_3$Na	15	176
PPy/PSSO$_3$	Equilibration after 59 mC reduction in PSSO$_3$Na	50	107
PPy/PSSO$_3$	Equilibration after 50 mC reduction in NaCl	15	175
PPy/PSSO$_3$	Equilibration after 57 mC reduction in HCl	15	17
PPy/PSSO$_3$	Equilibration after 50 mC reduction in CsCl	15	177
PPy/PSSO$_3$	Equilibration after 50 mC reduction in Et$_4$NCl	15	156
PPy/PSSO$_3$	Equilibration after 20 mC reduction in PSSO$_3$Na	15	14
PPy/PSSO$_3$	Equilibration after 30 mC reduction in PSSO$_3$Na	15	33
PPy/PSSO$_3$	Equilibration after 50 mC reduction in PSSO$_3$Na	15	176
PPy/PSSO$_3$/ClO$_4$ (1/5)	Equilibration after 90 mC reduction in PSSO$_3$Na	15	32
PPy/PSSO$_3$/ClO$_4$ (1/5)	Theoretical activity (90 mC)	—	700
PPy/PSSO$_3$	Equilibration after 90 mC reduction in PSSO$_3$Na	15	210
PPy/PSSO$_3$/ClO$_4$ (1/5)	Reduction *in situ*	—	66
PPy/PAA	Equilibration after 30 mC reduction in NaCl	15	24
PPy/PSSO$_3$	Equilibration after 30 mC reduction in NaCl	15	35

(acrylic acid) (PPy/PAA) instead of poly(styrene sulfonate). This study is expected to give some information on the effect of the stability of the ion pair on the binding efficiency for UO_2^{2+}.

The PPy/PAA resin was synthesized in an aqueous solution of PAA (0.01M; MW 2000; 19% neutralization) and pyrrole (1M) (current amount: 1 C; potential: 800 mV).[15] The film is very smooth and comparable to the previously prepared PPy/PSSO$_3$ films. The cyclic voltammogram (pH 3) shows that the film is reduced at -0.5 V [Fig. 3(A)], which corresponds to the incorporation of cations during reduction similarly to PPy/PSSO$_3$. However, since the carboxylic acid is a weak acid, the incorporated cation during the reduction at pH 3 should be H^+ rather than Na^+,
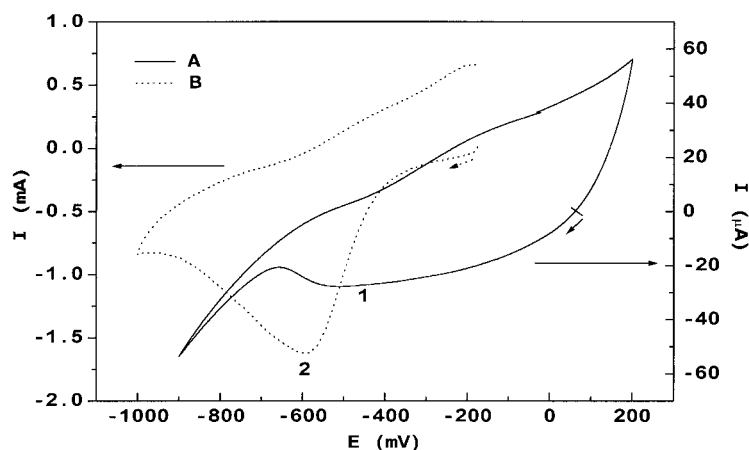

Figure 3 Cyclic voltammogram on a PPy/PAA film deposited onto Pt (scanning rate: 5 mV/s): (A) in 0.01M PAANa aqueous solution; (B) in 0.1M $UO_2(NO_3)_2$ aqueous solution; (1) reduction of PPy/PAA; (2) simultaneous reduction of PPy/PAA and UO_2^{2+}.

whereas only Na^+ is expected to be fixed at this pH by the sulfonated $PPy/PSSO_3$ resin. Uranyl incorporation is thus expected to be less important in the PPy/PAA resin compared to the $PPy/PSSO_3$ film.

The redox activity of the PPy/PAA film was analyzed in the $UO_2(NO_3)_2$ aqueous solution. The polymer reduction is obscured by reduction of the uranyl ions at -0.6 V [Fig. 3(B)]. Similarly to the $PPy/PSSO_3$ resins, the polymer is reduced simultaneously with UO_2^{2+}, so that the fixation must be carried out according to the two-step technique (Scheme 4).

Due to high pK_a, the carboxylic acid is protonated in the uranyl solution (pH 2.5).[16] The addition of imidazole to the solution allows the UO_2^{2+} solution to be prepared at pH 4. After reduction in the NaCl solution and equilibration in the UO_2^{2+} solution, the PPy/PAA film shows α-activity comparable to the $PPy/PSSO_3$ resin reduced with the same current quantity. Upon the assumption that at pH 4 approximately one-half of the carboxylic groups are protonated, the anionic site of the resin appears to have an effect on the UO_2^{2+} binding, carboxylate being more efficient than is sulfonate.

However, the capacity of the PPy/PAA resin seems to be lower than that of the $PPy/PSSO_3$ resin. Indeed, the current quantity needed to totally reduce the PPy/PAA film is smaller compared to $PPy/PSSO_3$. PPy would thus be less extensively doped by carboxylate anions than by sulfonate ones.

Complexation of the Uranyl Cation

The uranium fixation by the static-exchange process remains very low. It occurs slowly and independently of any potential control. However, for the binding-release cycle to be effective, the reduction of the UO_2^{2+} cation should be shifted to a more cathodic potential than is the reduction of the polymer. A possible strategy for reaching this purpose is to complex the UO_2^{2+} ions in solution. Nevertheless, the choice of the complexing agent must fulfill a series of criteria: electrochemical stability in the cathodic region, strong complexation of UO_2^{2+} in order to shift significantly the reduction potential, solubility in aqueous medium, lack of charge, and no major effect on the pH of the solution since the PPy electroactivity is altered in very acidic medium and uranyl hydroxide could precipitate at high pH.

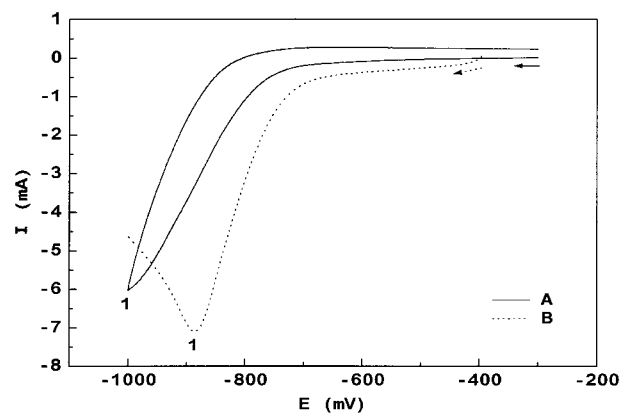*Complexation by PVI.* Complexation of UO_2^{2+} by PVI has already been traced by the shift of the

Figure 4 Cyclic voltammogram in $0.1M$ $UO_2(NO_3)_2$/$0.4M$ PVI aqueous solution (scanning rate: 5 mV/s): (A) on bare Pt; (B) on $PPy/PSSO_3$ film deposited onto Pt; (1) reduction of UO_2^{2+}.

maximum UV/VIS absorbance from 414 nm for the uncomplexed uranyl ion to 421 nm for UO_2^{2+} in the presence of PVI.[5] Since this complexation agent meets most of the requirements, it has been tested in this study.

The electrochemical stability of PVI in the cathodic region was confirmed in an aqueous solution of PVI ($0.08M$) and $NaNO_3$ ($0.1M$) as a conducting salt. The electrochemical behavior of $UO_2(NO_3)_2$ ($0.1M$) in the presence of an excess of complexation groups (PVI, $0.4M$) onto the Pt electrode was then studied. The reduction potential of uranyl is shifted down to -1 V onto platinum [Fig. 4(A)]. However, when a $PPy/PSSO_3$ film is substituted for Pt, a well-defined wave is observed at -0.88 V, which corresponds to the formation of a brown deposit of UO_2 on the polymer surface [Fig. 4(B)]. After washing, the experimental α-activity of the film is very low. The uranium is not attached to the resin, more likely because the uranyl/PVI complex has too large a size to be incorporated into the PPy resin.

Complexation by Imidazole. The polymeric complexing agent was changed for imidazole, which is expected to form a small-size uranyl complex that could be incorporated into PPy during reduction. The effect of imidazole on the electrochemical behavior of both PPy and UO_2^{2+} was investigated first since the behavior of PVI cannot be merely extrapolated to the constitutive complexing group.

Voltammetry of a $PPy/PSSO_3$ electrode in $0.1M$ imidazole/$0.1M$ $PSSO_3Na$ shows that the redox activity of the polymer is not perturbed by imidazole, the reduction occurring at -0.65 V/Pt. No
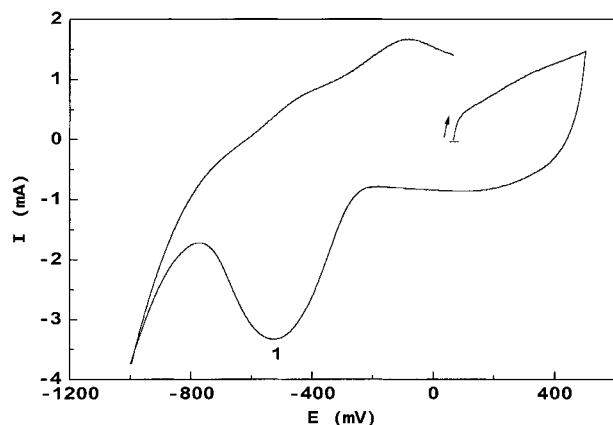
Figure 5 Cyclic voltammogram in 0.1M UO$_2$(NO$_3$)$_2$/ 0.1M imidazole aqueous solution on a PPy/PSSO$_3$ film deposited onto Pt (scanning rate: 50 mV/s): (1) simultaneous reduction of PPy/PSSO$_3$ and UO$_2^{2+}$ in UO$_2^+$.

uranyl precipitation is observed when one equivalent of imidazole is added to the UO$_2^{2+}$ solution, the pH of the imidazole aqueous solution being 8.5 compared to 4 for the UO$_2$(NO$_3$)$_2$ 0.1M/imidazole 0.1M mixture. The addition of two imidazole equivalents, however, results in a yellow precipitate attributed to uranium hydroxide.

Voltammetry of the UO$_2$(NO$_3$)$_2$ 0.1M/imidazole 0.1M solution on Pt shows that UO$_2^{2+}$ is reduced at -0.58 V/Pt followed by the solvent reduction. Comparison with the curve observed in the absence of imidazole shows that the reduction of UO$_2^{2+}$ into UO$_2$ (s) is inhibited. Furthermore, the UO$_2^{2+}$/UO$_2^+$ reduction peak is shifted to a less cathodic potential and its intensity is smaller. This reduction was not visible in the presence of PVI.

The voltamperometric curve was also recorded with a PPy/PSSO$_3$ electrode (Fig. 5). A wave at -0.5 V is observed with a higher intensity compared to the one recorded onto neat Pt. It was assigned to the simultaneous reduction of UO$_2^{2+}$ and the PPy film. During the reversed scan, PPy is reoxidized at -0.1 V. This reversibility is re-

producible as confirmed by the superposition of two successive cycles. Clearly, the uranyl reduction (UO$_2^{2+} \rightarrow$ UO$_2^+$) is influenced by the imidazole, since it becomes less cathodic and of a lower intensity. The second reduction [UO$_2^{2+} \rightarrow$ UO$_2$ (s)] is no longer observed, whereas the PPy reduction is not inhibited.

The uranium was tentatively fixed according to Scheme 3, and the α-activities are reported in Table VI. These values are clearly more important than are all the previous experimental α-activities, emphasizing the improved binding of uranium from this medium. The fixed uranium is incompletely released upon reoxidation of the film. An increased affinity of the UO$_2^{2+}$/imidazole complex for PPy could account for the partial release of these species.

Since imidazole appears to improve the extraction of uranium, the basic mechanism should be better understood. *A priori,* imidazole can either complex UO$_2^{2+}$ or increase the pH of the solution.

UV-vis spectroscopy was used to prove that the uranyl cation is complexed by imidazole. Imidazole has a hyperchromic effect on the absorption of uranyl, in contrast to the bathochromic effect observed in case of PVI. The addition of NaOH to the UO$_2^{2+}$ solution has the same hyperchromic effect. Moreover, if the UO$_2$(NO$_3$)$_2$/imidazole mixture is poured into an acidic solution (HNO$_3$), the initial absorption spectrum of UO$_2^{2+}$ is restored. In agreement with the scientific literature,[10] the uranyl absorption is low in contrast to the hydroxylated forms, such as [(UO$_2$)$_3$(OH)$_5$]$^+$ and [(UO$_2$)$_3$(OH)$_4$]$^{2+}$, that have a more intense absorption peak. These observations led to the conclusion that the key role of imidazole is to increase the pH rather than to complex the UO$_2^{2+}$ cations.

pH Effect

Consistently with the effect of imidazole, the voltamperometric curve of UO$_2^{2+}$ solutions changes upon addition of NaOH. Indeed, the first reduc-

Table VI α-Activity for Prereduced PPy/PSSO$_3$ Resin, Equilibrated in a Uranyl Nitrate/Imidazole Aqueous Solution

Resin	Electrochemical Treatment	Activity (Counts/10,000 s)
PPy/PSSO$_3$	Reduction 1 min at -0.8 V	395
PPy/PSSO$_3$	Reduction and reoxidation 1 min at -0.45 V	288
Pt	Reduction 1 min at -0.7 V	95

Table VII α-Activity for PPy/PSSO$_3$ Resin, Reduced in Uranyl Nitrate Solutions of Various pH

Solution	Electrochemical Reduction	Activity (Counts/10,000 s)
UO$_2$(NO$_3$)$_2$ 0.1M	$Qr = 300$ mC	65
UO$_2$(NO$_3$)$_2$ 0.1M/imidazole 0.1M	$Qr = 100$ mC	431
UO$_2$(NO$_3$)$_2$ 0.1M/NaOH 0.001M	$Qr = 100$ mC	60
UO$_2$(NO$_3$)$_2$ 0.1M/NaOH 0.005M	$Qr = 100$ mC	187
UO$_2$(NO$_3$)$_2$ 0.1M/NaOH 0.02M	$Qr = 100$ mC	262

tion peak is shifted to less cathodic potentials, its intensity is lower, and the second wave disappears (being masked by the solvent reduction) when the pH is increased. The first reduction wave can be reasonably attributed to the reduction of the hydroxylated complexes of UO$_2^{2+}$.

The uranium fixation is also improved by the addition of NaOH as assessed by the α-activity of PPy (Table VII). However, this improvement is less important when NaOH is used instead of imidazole at the same pH, which indicates that precipitation of the hydroxylated species is not basically at the origin of the α-activity. Formation of hydroxylated uranyl species is supposed to decrease the amount of UO$_2^{2+}$, which is favorable to the reduction of the polymer resin. The better results promoted by imidazole can be explained by the less important competition for fixation between protonated imidazole and UO$_2^{2+}$ compared to Na$^+$ and UO$_2^{2+}$.

Fixation of Negatively Charged Complexes

Although the direct synthesis of PPy in the UO$_2$(NO$_3$)$_2$ solution leads to electroactive PPy, no α-activity is observed for these films, at pH 4 (with imidazole), indicating that the incorporation of possible negative complexes[17] of UO$_2^{2+}$, that is, [UO$_2$(NO$_3$)$_3$]$^-$, is negligible, as result of competition with the nitrate anions for the PPy doping. It is noteworthy that after a short period of time (ca. 2 h) the solution turns from yellow to green. Since UO$_2^{2+}$ is able to oxidize pyrrole, it can also oxidize reduced PPy. The PPy film is thus a possible catalytic mediator for the preparation of tetravalent uranium by reduction of UO$_2^{2+}$. Indeed, when the reduced PPy film is dipped into the uranyl nitrate solution, PPy$^+$ and U (IV) are formed as result of the UO$_2^{2+}$/PPy^0 redox reaction. When PPy is completely oxidized, it can be reduced again in a separate bath and immersed in the UO$_2^{2+}$ solution in order to form U (IV) quantitatively. This system can thus find application as a catalytic mediator for the preparation of aqueous solutions of reduced metallic ions or as stabilizer of these oxidizable solutions.

CONCLUSIONS

PPy/PSSO$_3$ cationic resin appears to be a better candidate than is PPy/ClO$_4^-$ for uranium fixation. The control of pH is very important in order to preserve the electroactivity of the PPy resin.

UO$_2^{2+}$ can be fixed by the PPy/PSSO$_3$ resin but the efficiency is low (4%), since the cation reduction competes with the polymer reduction. The static fixation process based on a prereduced PPy film is poorly efficient since the equilibrium time is limited by the resin reoxidation.

Although the system could be improved by combining PPy with PAA rather than with PSSO$_3$, the control of pH is still more delicate in this case. Competition between H$^+$ and UO$_2^{2+}$ limits the final α-activity of the PPy films.

Complexation of UO$_2^{2+}$ cations is a possible strategy to improve the fixation, and imidazole is a valuable complexing agent since it increases substantially the amount of uranium fixed to PPy. Still better efficiency could result from the grafting of PVI onto PPy. However, the specificity of the complexing agent for one (or few) species may be a limitation on the scope of these systems.

Finally, the use of a conducting polymer that would be reduced at a less cathodic potential than is PPy is another way to improve the efficacy of the PPy/PSSO$_3$ resins. Polyaniline, which has to be doped by a polyanion in order to form a cationic resin, is under current investigation.

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