

Electrochemical study of uranium exchange on a polypyrrole resin

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Abstract:

The ability to electrochemically control the binding of uranium ions by redox active polypyrrole resins has been studied. The optimization of the conditions for the fixation of uranium has been defined while taking in account the nature of the fixed species, the nature of the resin and the nature of the solutions.

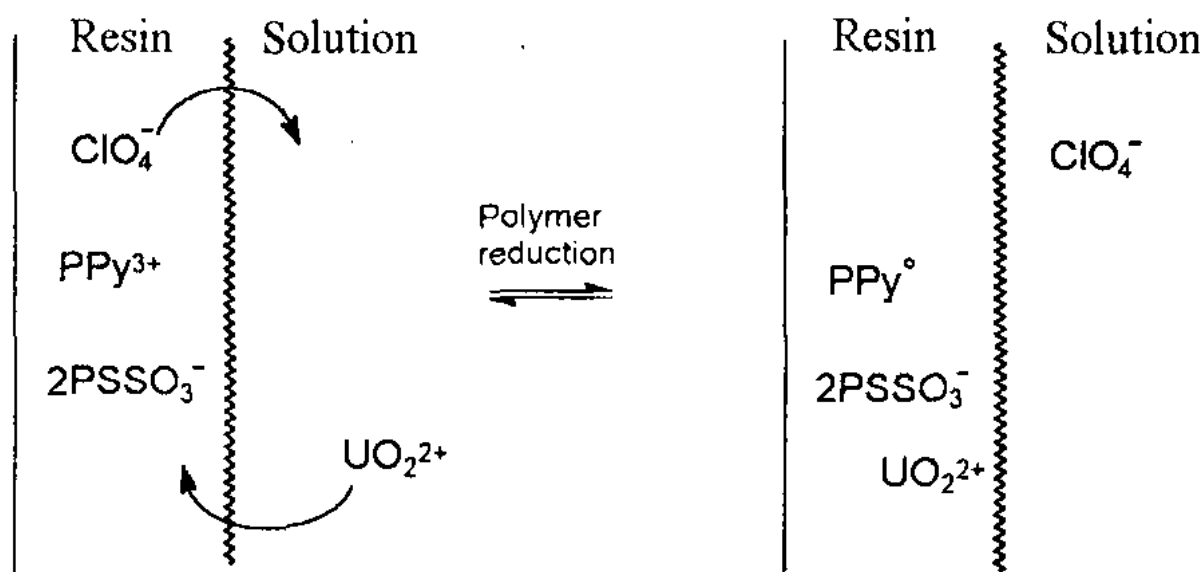
Introduction

The treatment of low level activity radioactive wastes by organic polymers receives today an increasing attention.¹ In this field, an original path consists in developing a reversible process where ions can be fixed or released by applying a specific potential value.²

The development of electronically conducting polymers which is a novel class of electroactive polymers,³ offers new promising materials for such a potential-controlled process. Indeed, during a redox cycle, the reduction and the reoxidation of these polymers occur simultaneously to ion exchange between the solution and the polymer film as described below.

Depending on the size of the anions that are incorporated during the polymer synthesis, we can obtain two types of resins: with small size anions, it comes that an anionic resin is achieved since the exchanged species are anions (Scheme 1). On the other hand, when a polymeric anion like polystyrene sulfonate (PSSO₃⁻) is used, the entanglement of the conducting polymer chains and PSSO₃⁻ chains prevents the release of anions. The result is that cations are exchanged during the electrochemical redox process (Scheme 1).

Scheme 1



Polypyrrole (PPy) appears as a good candidate for such a resin since it is stable, electroactive and insoluble in aqueous medium. Moreover, it can be electrochemically synthesized in the same medium. The ability of that kind of polymer to fix and release anions (Cl^- , ClO_4^- , ...) ⁴⁻⁵ and cations (Th^{4+} , La^{3+} , Cs^+ , Ba^{2+} , ...) ^{2,6} has already been described. These cations are not reducible to the metallic state in water and no intermediate oxidation state (i.e. Th^{3+} , La^{2+} or Ba^+) is known. Thus, the interaction between these cations and a PPy polarized resin is only an electrostatic process. This process no longer holds in the case of UO_2^{2+} and U^{4+} cations since an intermediate oxidation state is known and furthermore the electrochemical reduction of UO_2^{2+} to $\text{UO}_2(\text{s})$ is achieved in water within some well-defined conditions. ⁷

In this paper, we have analyzed the ability of both anionic and cationic polypyrrole resins to fix uranium ions from various solutions.

Experimental

$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was delivered by Fluka. Bidistilled water was used as solvent after being purged with nitrogen. Pyrrole (Aldrich) was freshly distilled under reduced pressure before use. Imidazole (Aldrich), PSSO_3Na (Aldrich MW 70000), and LiClO_4 (Aldrich) were used as received. Polyvinylimidazole (MWy 30000) was obtained by radical polymerization of vinylimidazole (Aldrich) in ethanol using AIBN (Acros) as initiator. ⁸

The 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 nitrogen atmosphere in a closed cell, using platinum (1 cm^2) or glassy carbon (1.5 cm^2) as working electrode and a platinum sheet as counter electrode. A platinum sheet was also used as a pseudoreference.

The electrochemical synthesis of polypyrrole was achieved potentiostatically ($E_S = +0.7\text{ V/Pt}$) in aqueous solutions of LiClO_4 (0.1M) or PSSO_3Na (0.1M) and pyrrole (0.1M) at room temperature.

Alpha-counting was carried out with a VEMI counter working at 1400 mV during 10000 seconds.

Results and discussion

The investigation was started using Cs_2UCl_6 (6M HCl) and UCl_4 aqueous solutions in order to study the fixation of both an anion (UCl_6^{2-}) and a cation (U^{4+}). However, the very low pH of both solutions ($\text{pH} < 1$) alters the redox activity of the PPy resins (PPy/ClO_4^- and PPy/PSSO_3^-) and no uranium can be fixed from these media. The use of a decimolar aqueous solution of uranyl nitrate ($\text{pH } 2.5$) has thus been preferred. Fixation of the UO_2^{2+} species was carried out by reduction of the PPy/PSSO_3^- resin. In this case, however, the reduction of the uranyl cation competed with the PPy/PSSO_3^- reduction. ² Two different paths have consequently been investigated in order to avoid this interfering reduction.

Static fixation

To avoid the uranyl reduction, the PPy/PSSO_3^- resin was prereduced in a bath containing only an electrochemically stable conducting salt (NaPSSO_3 , CsCl or Et_4NCl); the prereduced film was then dipped into the uranyl nitrate solution. After equilibration, alpha counting of the electrode allowed the quantification of the fixed uranium (Table 1).

Various parameters were studied in order to optimize the fixation conditions. The best equilibrium time has been found to be 15 minutes which is a good compromise between the reduced PPy stability and the uranium fixation.

The nature of the exchanged cation has also an influence on the efficacy of the uranyl binding while a weak effect of the ion charge density has been observed as it appears from the comparison of the results obtained with Na^+ and with Cs^+ cations (Table 1). The exchange with an organic cation such as Et_4N^+ is, however, in favor of this cation. The slower diffusion of this organic cation in the PPy film than that of UO_2^{2+} limits the incorporation of the radioactive cation.

Finally, the effect, of the stability of the ion pair on the UO_2^{2+} fixation has been studied by using a PPy film doped with polyacrylic acid (PAA) instead of polystyrene sulfonate. After equilibrium in the UO_2^{2+} solution of the film prereduced in NaCl, the activity was similar to the one obtained with the PPy/PSSO₃⁻ resin. At the fixation pH, more than the half of the anionic sites are protonated since the carboxylic function of PAA is a weak acid and one can conclude that the use of PAA has an effect on the uranyl binding leading to an improvement of the UO_2^{2+} incorporation.

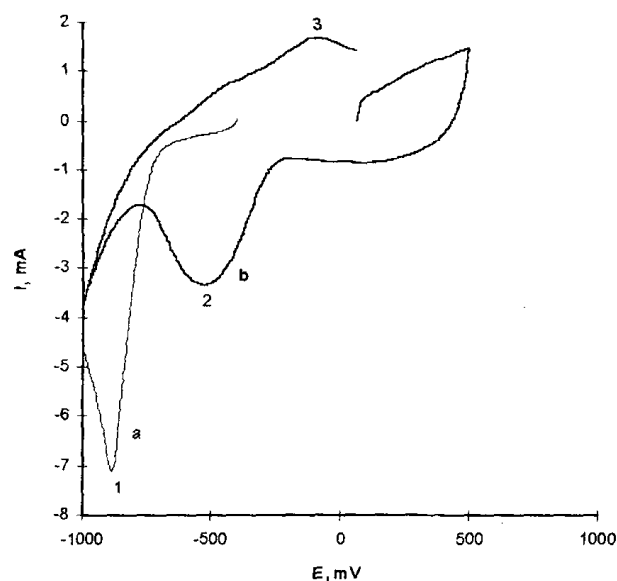
Table 1. Alpha-activities measured onto a prereduced PPy/PSSO₃ resin in various conditions and equilibrated in a uranyl nitrate solution

Nature of the resin	Electrochemical treatment	Qr , mC	t_{eq} , min	Activity, counts/10,000 s
PPy/PSSO ₃ ⁻	Reduced in PSSO ₃ Na	50	5	57
PPy/PSSO ₃ ⁻	Reduced in PSSO ₃ Na	50	15	176
PPy/PSSO ₃ ⁻	Reduced in PSSO ₃ Na	59	50	107
PPy/PSSO ₃ ⁻	Reduced in CsCl	50	15	176
PPy/PSSO ₃ ⁻	Reduced in Et ₄ NCl	50	15	156
PPy/PAA	Reduced in NaCl	50	15	174

Table 2. Alpha-activities measured onto a PPy/PSSO₃ resin reduced in a decimolar uranyl nitrate solution with various additives

Nature of the resin	Composition of the fixation bath	Qr , mC	Activity, counts/10,000 s
PPy/PSSO ₃ ⁻	$\text{UO}_2(\text{NO}_3)_2/0.4\text{M PVI}$	300	23
PPy/PSSO ₃ ⁻	$\text{UO}_2(\text{NO}_3)_2/0.1\text{M imidazole}$	100	431
PPy/PSSO ₃ ⁻	$\text{UO}_2(\text{NO}_3)_2$	300	65
PPy/PSSO ₃ ⁻	$\text{UO}_2(\text{NO}_3)_2/0.001\text{M NaOH}$	100	60
PPy/PSSO ₃ ⁻	$\text{UO}_2(\text{NO}_3)_2/0.005\text{M NaOH}$	100	187
PPy/PSSO ₃ ⁻	$\text{UO}_2(\text{NO}_3)_2/0.02\text{M NaOH}$	100	262

Fig. 1. (a) Voltammogram of the PPy/PSSO₃⁻ film in 0.1 M $\text{UO}_2(\text{NO}_3)_2/0.04\text{M PVI}$ solution, (1) UO_2 formation; (b) Cyclic voltammogram onto PPy/PSSO₃⁻ film in 0.1 M $\text{UO}_2(\text{NO}_3)_2/0.1\text{M imidazole}$ (2) simultaneous reduction of PPy/PSSO₃⁻ and of UO_2^{2+} to form UO_2^+ , (3) PPy/PSSO₃⁻ reoxidation



Complexation of the uranyl cation

The radioactivity fixed by the static exchange process shows the ability of that kind of resin to exchange cations, however the measured activities remain very low. If we want to keep the potential as a regulator of the binding-release cycles, the reduction of the UO_2^{2+} cation had to be damped with respect to the polymer reduction. A possible strategy to overcome this problem is to complex the UO_2^{2+} ion in solution in order to shift its reduction potential towards a more cathodic value than that of the polymer.

Polyvinylimidazole complexation: The complexation of UO_2^{2+} cation by the polyvinylimidazole (PVI) has already been evidenced in a previous paper.⁹ This neutral ligand allows the formation of a complex that is still positively charged which is a required condition for the described fixation process.

We have verified the cathodic stability of PVI with a solution containing only 0.08M PVI and a conducting salt (0.1 M NaNO_3). Moreover, the voltammetry of UO_2^{2+} complexed by PVI (0.1 M $\text{UO}_2(\text{NO}_3)_2$ and 0.4M PVI, i.e., 37.6 g/l), recorded with a Pt indicating electrode, shows that the UO_2^{2+} reduction wave is shifted down to -1 V. However, when scanning on the PPy/PSSO_3^- film, 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. 1a). After rinsing, the measured α -activity of the film is very low. The uranium is thus not fixed by the resin. In fact, the uranyl/PVI polymeric complex has too large size to be incorporated in the PPy resin.

Imidazole complexation: The polymeric complexing agent was so far changed for the imidazole complexing unit as to reduce the size of the uranyl complex allowing then its incorporation during the reduction. The addition of one equivalent of imidazole to the UO_2^{2+} solution does not lead to uranyl precipitation while the pH of the imidazole aqueous solution is 8.5. The pH of the mixture 0.1M $\text{UO}_2(\text{NO}_3)_2$ /0.1M imidazole equaled 4. The addition of two equivalents of imidazole leads however to the formation of a yellow precipitate attributed to uranium hydroxide.

The voltammetry of the 0.1 M $\text{UO}_2(\text{NO}_3)_2$ /0.1M imidazole solution on a Pt electrode evidences a reduction of UO_2^{2+} at -0.58 V/Pt followed by the reduction of the solvent. If we compare this curve with the one obtained without imidazole, the second reduction has disappeared i.e. the UO_2 (s) formation is inhibited. The $\text{UO}_2^{2+}/\text{UO}_2^+$ reduction peak is shifted to a lower cathodic potential and its intensity is also lower. However, a reduction is now visible while there was no peak with PVI.

The voltammetric curve has been recorded on a PPy/PSSO_3^- film (Fig. 1b) plunging in the same bath. A wave at -0.5 V is observed with a higher intensity than on bare Pt and this increased value is attributed to the simultaneous reduction of both UO_2^{2+} and of the PPy film. During the reversed scan, the reoxidation of the polymer is observed at -0.1 V. Two successive cycles are well superimposed: the reversible process appears to be reproducible. We can conclude that the uranyl reduction is influenced by the presence of imidazole in the bath; the first cathodic reduction appears to be less cathodic but with a lower intensity and the reduction of the PPy is not inhibited by this reaction. The second reduction $\text{UO}_2^+ + \text{e}^- \rightarrow \text{UO}_2$ (s) which was observed without imidazole, has disappeared.

The fixation of uranium is carried out in situ and the corresponding α -activities are reported in Table 2. The value with imidazole is clearly more important than all the previous measured activities showing the improvement of the binding of uranium from this medium.

Since the use of imidazole appears to improve the amount of extracted uranium, the role of imidazole in the whole process has been investigated. In fact, imidazole can be considered either as a complexing agent or as a base. UV-VIS spectroscopy has been used to evidence the complexation of the uranyl cation by imidazole. The presence of imidazole leads to an hyperchromic effect on the absorption peak of the uranyl but no bathochromic effect has been observed contrary to the case of PVI. The same hyperchromic effect is, however, observed by adding NaOH to the UO_2^{2+} solution. As described in the literature,⁷ the uranyl ion has a weak absorption while its hydroxylated forms like $[(\text{UO}_2)_3(\text{OH})_5]^+$ and $[(\text{UO}_2)_3(\text{OH})_4]^{2+}$ have a more intense absorption peak.

These observations lead to the conclusion that the imidazole has to be considered as a base rather than a complexing agent for the UO_2^{2+} cation.

We just demonstrate the improvement obtained by the imidazole addition and its effect on the pH of the fixation bath. When NaOH is added to the UO_2^{2+} solution, the evolution of the voltamperometric curves is similar to the evolution observed with imidazole. The fixation is also improved in this bath if we compare the measured

activity with the same value obtained without NaOH (Table 2). However, in presence of NaOH the amount of fixed uranium is less important than with imidazole at the same pH value. We can thus suppose that the formation of hydroxylated species of uranyl decreases the amount of available UO_2^{2+} allowing so the better reduction of the polymer resin. In this case, the best results observed for the imidazole bath are explained by a lower competition for the fixation between large size protonated imidazole and UO_2^{2+} than between Na^+ and UO_2^{2+} cations.

Conclusions

The use of a PPy/PSSO_3^- cationic resin appears to be more suitable for the uranium fixation than the PPy/ClO_4^- . The control of the pH of the solution is very important in order to keep the electroactivity of the PPy resin.

UO_2^{2+} can be fixed by PPy/PSSO_3^- resin but the efficacy is low (4%) since the reduction of the cation competes with the polymer reduction. The static fixation process of a prereduced film does not allow higher activities since the equilibrium time is limited by the resin reoxidation.

An improvement of the system could be achieved by using a PPy/PAA resin rather than a PPy/PSSO_3^- resin; however, the control of the pH of the bath is more important in this case. The competition between H^+ and UO_2^{2+} limits the fixed activity.

Complexation is a partial answer to improve the fixation and imidazole is a good candidate. A real improvement of the fixation of uranium in the presence of imidazole has been observed. Better results should be achieved by grafting the PVI onto the PPy chains. However, it must be borne in mind that the use of a complexing agent is specific to the species that had to be fixed. This fact gives a limit of the application field of the system.

An improved system should be achieved using another conducting polymer which is less reduced cathodically. We propose the use of a polyaniline which had to be doped with a polyanion in order to give a cationic resin. The behavior of these different conducting resins are now under investigation.

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