

« Electrodeposition of actinides in room temperature ionic liquids »

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1. Project Goals

Ionic Liquids (ILs) are salts with a melting point below 100°C. Their physico-chemical properties can be tuned by a suitable choice of the anion/cation combination. Neither volatile nor flammable, ILs could be a “green” alternative for actinides and lanthanides separation processes based on electrodeposition. They are then very attractive for both radiochemists and nuclear physicists. Indeed, the future nuclear industry needs:

- 1) Innovative spent nuclear fuel reprocessing to minimize radioactive waste. ILs could be used as replacement for organic solvents used in PUREX technology or as medium for separation by electrodeposition.
- 2) Radioactive oxygen-free targets for specific measurements in nuclear physics.

However, fundamental data on actinides and lanthanides in ILs are rather scarce. Using ILs as electrochemical solvents in nuclear fuel cycle requires data collection about redox properties of actinides and lanthanides in these media. Therefore the work has been first focused on the redox properties of two lanthanides, neodymium and lanthanum, in ILs. The main goals are:

- To select by electroanalysis the experimental conditions for electrodeposition of neodymium and lanthanum;
- To carry out the electrolysis and to characterize the deposit (composition and morphology);
- To determine the mechanism of electrodeposition.

2. Work achieved

ILs based on the bis(trifluoromethylsulfonyl)imide anion ($((CF_3SO_2)_2N^-$, noted TFSI) have recently gained a growing of interest because of their hydrophobic character, their superior chemical and thermal stability, their low viscosity, low melting point, high conductivity and high radiolytic stability. All of these criteria are very important for electrodeposition of actinides and lanthanides, known to be very electropositive elements. These TFSI - based ILs have then been selected to study the electrodeposition of neodymium and lanthanum. The work has been focused on the $Nd(TFSI)_3$ and $La(TFSI)_3$ salts, which are very water sensitive. Moreover, the redox properties of both ILs and metallic salts depend on the water content. All experiments have then been carried out in an argon – filled dry box ($H_2O < 10$ ppm ; $O_2 < 1$ ppm).

2.1. Electrodeposition of neodymium in ILs

The electrochemical behavior of Nd(III) has been first studied by cyclic voltammetry in three TFSI based ILs: the 1-butyl-3-methylimidazolium ($[BuMeIm]^+$), the methyl-tributylammonium ($[MeBu_3N]^+$) and the butyl-methylpyrrolidinium ($[BuMePyr]^+$). The influence of the electrode material has also been investigated: platinum (Pt), gold (Au), glassy carbon (GC) and boron doped diamond (BDD) at 25 and 60 °C.

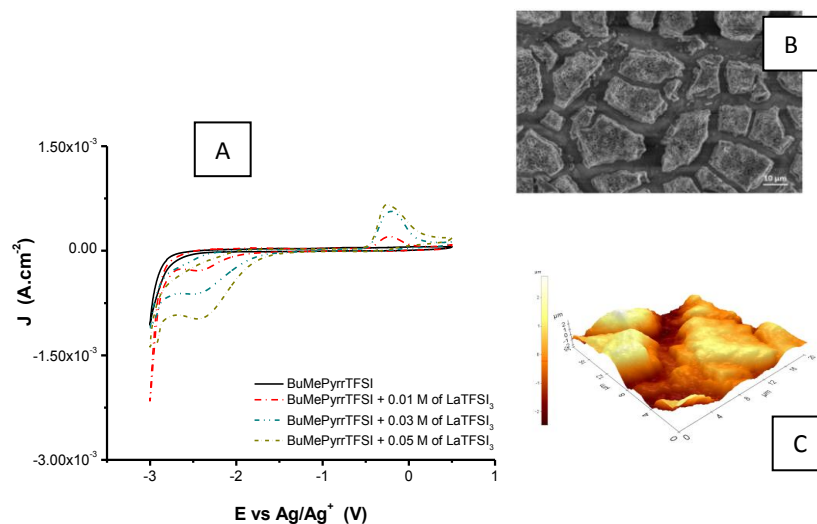
The results show that Nd(III) is reduced at very negative potential. Since the imidazolium cation is reduced before Nd(III), the electrodeposition of neodymium could not be achieved in the $[BuMeIm][TFSI]$ IL. Moreover, the electroanalysis has put in evidence that ammonium IL contains impurities that could be reduced in the same potential range that the reduction potential of Nd(III). Finally, the reduction of Nd(III) could only be observed in the $[BuMePyr][TFSI]$ IL at Pt, Au, GC and BDD electrodes.

Therefore, the quantitative electrolysis have then been carried out in the $[BuMePyr][TFSI]$ IL. The formation of a black deposit has been observed at the electrode surface. Unfortunately, this deposit is also observed in absence of the Nd(III) salt. This result means that in our experimental conditions the neodymium(III) cannot be reduced selectively because its reduction potential is near the pyrrolidinium reduction potential.

2.2. Electrodeposition of lanthanum in ILs

The electrochemical behavior of La(III) has been also studied by cyclic voltammetry in the three TFSI based ILs at 25 and 60°C. The reduction process of La(III) could only be observed at platinum electrode. The results obtained by cyclic voltammetry show that the redox properties of La(III) depends on the IL. While in $[BuMePyr][TFSI]$ and $[BuMeIm][TFSI]$ ILs, one cathodic is detected respectively at -2.42 and -1.85 V, in $[MeBu_3N][TFSI]$ IL, two cathodic peaks are observed at -2.1 and -2.4 V (see for example in

the figure 1 (curve A) the cyclic voltammogram of $\text{La}(\text{TFSI})_3$ in $[\text{BuMePyr}][\text{TFSI}]$. Electroanalysis is still in progress to understand the redox mechanism as a function of the IL. For all ILs, at the reverse scan, a redissolution peak is observed putting in evidence the formation of a deposit at the electrode surface.



A) Cyclic voltammograms of BuMePyr with different quantities of La^{3+} with the correspondent B) SEM and C) AFM images of the coating obtained after 3h of electrodeposition at $-2.35 \text{ V vs Ag}/\text{Ag}^+$.

Electrolysis at controlled potential have then been conducted in the three ILs at Pt electrode during three hours. The presence of lanthanum inside the deposit has been proved by XRF (X Ray Fluorescence, CEA Saclay). The chemical composition has also been determined by EDX (CSNSM, Orsay). The presence of lanthanum is confirmed and C, O, S, N and F, probably attributed to the insertion of the IL, could also be detected.

The coating morphology has been examined by SEM (CEA Saclay and CSNSM Orsay). In $[\text{BuMePyr}][\text{TFSI}]$ and $[\text{MeBu}_3\text{N}][\text{TFSI}]$ ILs, we can observe grain islands around $20 \mu\text{m}$ of diameter and nanoparticles layer generated certainly at the first stage of the electrodeposition (see for example figure 1 curve B, the SEM micrograph of the deposit obtained in $[\text{BuMePyr}][\text{TFSI}]$). By calcination, SEM analysis shows that the ILs ions have been removed from the coating and single nanoparticles have been observed. In $[\text{BuMeIm}][\text{TFSI}]$ IL, a smooth flat surface is observed.

The nucleation/growth process during the electrodeposition has also been studied at short times. Chronoamperometric experiments show that lanthanum nucleation/growth process is carried out in an instantaneous way while AFM analysis (CACAO installation, Orsay) showed that it occurs by a progressive one. Same differences were already described in literature. Then, we can propose that a cause of the strong coulombic attraction created by initial crystals, instantaneous nucleation/growth process can form a dendritic surface.

The mechanism of electrodeposition including the nucleation/growth process is still in progress. Nevertheless, a manuscript is being prepared for publication.

3. Publications

“Electrodeposition of lanthanum in the room temperature ionic liquids”

Servando López-León, Veronika A. Zinovyeva, Céline Cannes, Claire Le Naour, Charles-Olivier Bacri, Jaques de Sanoit, Céline Gesset, Dominique Chambellan.

Poster presented at the Euechem2014 congress, Tallinn (Estonia) 6 – 11 July 2014.

“Electrodépôt de lanthane dans des liquides ioniques hydrophobes : Mécanisme et croissance de dépôt”.

Servando López-León, Céline Cannes, Veronika A. Zinovyeva, Claire Le Naour, Charles-Olivier Bacri, Jaques de Sanoit, Céline Gesset, Dominique Chambellan.

Oral communication presented at the Journées Nationales de Radiochimie et de chimie Nucléaire 2014, Orsay (France) 11 – 12 september 2014.

4. Relevance of the project within P2IO

This interdisciplinary project has created a strong synergy between laboratories of P2IO: IPNO, CSNSM and CEA. The scientific expertise such as radiochemistry, electrochemistry and surface characterization, available in the P2IO framework has allowed one to determine the experimental conditions and the mechanism of lanthanum electrodeposition. This work is a first step to find experimental conditions for electrodeposition of lanthanides and actinides at the metallic state. This is a real challenge to prepare radioactive oxygen-free targets for nuclear physics measurements.