Ecole Doctorale 534 MIPEGE

Modélisation et Instrumentation en Physique, Energies, Géosciences et Environnement

Université Paris-Sud 11

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Sujet de thèse 2012 proposé

Laboratory : Institut de Physique Nucléaire d'Orsay

Group : radiochemistry group

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Title : « Electrodeposition of actinides in room temperature ionic liquids »

Proposal :

Water-stable Room Temperature Ionic Liquids (RTILs) are solvents entirely composed of organic cations and organic or inorganic anions. RTILs exist in liquid state at temperatures lower than 100°C and are neither volatile nor flammable which makes them "green solvents". Moreover, their physico-chemical properties, such as hydrophobicity and high stability towards oxidation and reduction, can be tuned by a suitable choice of the anion/cation combination. Consequently, this medium is really suitable as an alternative for actinides separation processes based on electrodeposition. That makes thus these hydrophobic RTILs very attractive for both radiochemists and nuclear physicists. Indeed, the future nuclear industry needs:

1) Innovative spent nuclear fuel reprocessing in order to minimize radioactive waste. In that case, RTILs could be used as replacement for volatile organic solvents used in PUREX technology or as medium for separation by electrodeposition.
2) Radioactive oxygen-free targets for transmutation cross section measurements. The main goal of the CACAO project (Chimie des Actinides et Cibles radioActives à Orsay) is an installation for the preparation and characterization of thin radioactive layers.
However, although the RTILs properties are widely studied, fundamental data on actinide chemistry in these media are rather scarce. Using RTILs as electrochemical solvents in nuclear fuel cycle requires therefore data collection about solvation, complexation, redox properties and coordination chemistry of actinides (and lanthanides) in these media.
On the one hand, the research program will be focused on the speciation of uranium and lanthanides in RTILs in presence of different kinds of ligands, in order to find experimental conditions for their solubilisation and stabilization in these media. A particular attention will also be paid to the hydrolysis of actinides (especially at the +IV oxidation state). Indeed, An(IV) display a strong tendency towards hydrolysis and the chosen ionic liquids, although hydrophobic, may contain some water.
On the other hand, the work will concern the electrochemical behavior of the uranium and lanthanides complexes. Several parameters will be examined: the RTIL nature, its water content, the chemical form and the oxidation state of the initial actinide complex, the electrode material. Indeed, in the particular case of the CACAO project, the type of the electrode (carbon, aluminium, platinum…) and its thickness has to be considered in order to optimize the thin radioactive film adhesion on the backing. The redox process would be elucidated by voltammetry and impedancemetry and then the experimental conditions of the electrodeposition will be optimized.

The results obtained by electroanalysis will then be used to prepare thin layers by macroelectrolysis. A pre-treatment of the backing has also to be considered to activate the surface and favour the electrodeposition. The radiochemistry group together with the nuclear physicists involved in the CACAO project will develop appropriate nuclearized techniques for characterizing both the liquid-solid interfaces (between the radioactive electrolyte and the targets backing) and the deposit (chemical composition, stability, adherence, thickness and homogeneity).

Equipments :
Gloves boxes (one of them being under inert atmosphere), electrochemical stands, techniques of surface characterization (SECM, AFM, α cartography, autoradiography), techniques of spectroscopy (UV-visible absorption, IR, TRLS), microcalorimetry and α, β, γ spectrometry.

National and international collaborations:

CEA Saclay ; LISE (UPR 15 de l'Université P. et M. Curie) ; l'IRMM de Geel et l'Université de Mayence.

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