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Electrochemical and spectroscopical investigation of uranium in room-temperature ionic liquids

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Room-temperature ionic liquids (RTILs) consist of organic cations and organic or inorganic anions. Beside their fluidity over a large temperature range, they have versatile physical and chemical properties, e.g. low vapour pressure, thermal and chemical stability [1]. In our investigation, the wide electrochemical window of RTILs is of particular importance. RTILs are considered as “green solvents” and may open up new options in industrial actinide separation [2].

This work is about the redox behaviour of hexavalent uranium in 1-butyl-3-methylimidazolium based RTILs. Two different methods have been used: cyclic voltammetry to achieve information about the redox behaviour of uranium(VI) and electrochemical deposition to get samples for X-ray photoelectron spectroscopy (XPS). In both cases the same uranium RTIL solutions have been used. Uranium oxalate (UO₂C₂O₄) has been dissolved in

1-butyl-3-methylimidazolium methylsulfate (BmimMsu) and 1-butyl-3-methylimidazolium thiocyanate (BmimSCN) under argon atmosphere. Afterwards the solutions

(c(U) ~ 8•10⁻³ mol/L) have been dried under reduced pressure and heating to minimize the water content in these stock solutions. The amount of water has been determined via Karl-Fischer titration (≤ 10 ppm).

For the cyclic voltammetric measurements glassy carbon has been used as working electrode, titanium as counter electrode and platinum as quasi-reference electrode (versus ferrocene/ferrocenium). All experiments have been carried out under argon atmosphere. BmimMsu and BmimSCN provide an electrochemical window of 4.5 –5.0 V, therefore the reduction of U(VI) to U(IV) should be possible. Actually for both UO₂C₂O₄ RTIL solutions cyclic voltammograms have been achieved, which showed a similar progression with a shift of the redox potentials. The cyclic voltammograms suggest a quasi-reversible reduction of uranium(VI) to uranium(IV). The potentials for the U(VI)/U(IV) reduction in BmimMsu and BmimSCN were -1.9 mV and -2.0 mV (vs. SHE), respectively.

To verify the reduction of U(VI) to U(IV), samples have been prepared under argon atmosphere for XPS measurements. The uranium was deposited on a titanium foil applying a potential of 2 V for 3 h. The measured binding energies for the U 4f and U 5f XPS-lines confirm the reduction of hexavalent uranium to the tetravalent oxidation state.

By combining two different methods, it was possible to demonstrate that U(VI) can be reduced to U(IV) and deposited as tetravalent uranium on titanium foils using RTILs as solvent.

Literature:

[1] K. Binnemans, Lanthanides and actinides in ionic liquids, Chem. Rev. 2007, 107, 2592-2614

[2] A.E. Visser, R.D. Rogers, Room-temperature ionic liquids: new solvents for f-element separations and associated solution chemistry, J. Solid State Chem. 2003, 171, 109-113

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