Cyclic voltammetric study of uranium in room-temperature ionic liquids

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Introduction: 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, thermical 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].
The redox behaviour of hexavalent uranium in 1-butyl-3-methylimidazolium based RTILs has been studied, using cyclic voltammetry to achieve information about the redox couple $U^{(+VI)}/U^{(+IV)}$ in the bulk solution.

Experimental: In both cases uranium oxalate ($UO_2C_2O_4$) has been dissolved in 1-butyl-3-methylimidazolium methylsufate (BmimMsu) and 1-butyl-3-methylimidazolium thiocyanate (BmimSCN) under argon atmosphere. Afterwards the solutions (c(U) ~ $8 \cdot 10^{-3}$ 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 E^0 = 400 mV (versus SHE)[3]). All experiments have been carried out under argon atmosphere and room-temperature.

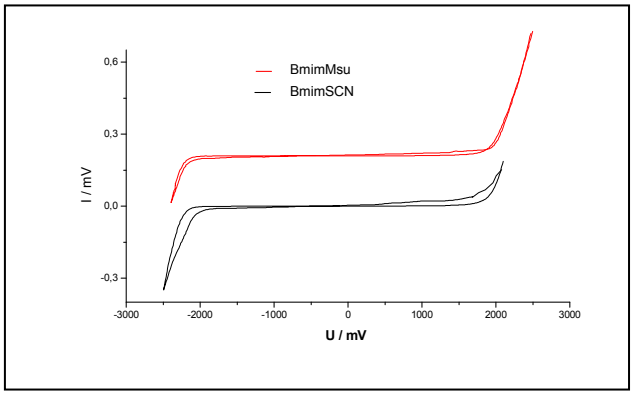

Figure 1 : Cyclic voltammogram of BmimMsu and BmimSCN

Results: BmimMsu and BmimSCN provide an electrochemical window of 4.5 – 5.0 V (Fig. 1), therefore the reduction of $U^{(+VI)}$ to $U^{(+IV)}$ should be possible. Actually for both $UO_2C_2O_4$-RTIL solutions cyclic voltammograms have been achieved, which showed a similar progression with a shift of the redox potentials (Fig. 2).

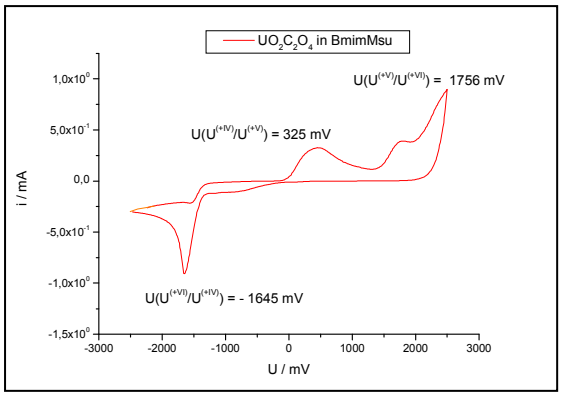

Figure 2 : Cyclic voltammogram of the $UO_2C_2O_4$-BmimMsu solution (versus ferrocene/ferrocenium)

With the help of the peak location, it is possible to identify a quasi-reversible reduction of uranium(VI) to uranium(IV) with an uranium(V) species as intermediate. The anodic peak potential for the $U^{(+IV)}/U^{(+V)}$ oxidation is comparable to the measurements in $BmimTf_2N$ [4] and the anodic peak potential for the $U^{(+VI)}/U^{(+IV)}$ reduction to the measurements in BmimCl [5]. A further criterion for a quasi-reversible process, is the linear relationship between the cathodic peak current and the root of the scan rate of the measurements (v = 1 – 100 mV/s) [6]. The potentials for the U(VI)/U(IV) redox couple are shown in Table 1 for both systems (BmimMsu and BmimSCN).

	Peak potential U [mV]	
Redox couple	$UO_2C_2O_4$-BmimSCN	$UO_2C_2O_4$-BmimMsu
$U^{(+VI)}/U^{(+IV)}$	-2087	-1911
$U^{(+IV)}/U^{(+V)}$	-96	59
$U^{(+V)}/U^{(+VI)}$	1066	1490

Table 1 : Potentials of the uranium redox couples (versus SHE)

References

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