SCIENCE CHINA
Chemistry

• ARTICLES •
September 2012 Vol.55 No.9: 1699–1704
• SPECIAL TOPIC • Nuclear Fuel Cycle Chemistry
doi: 10.1007/s11426-012-4693-8

Electrochemical behavior of $[UO_2Cl_4]^{2-}$ in 1-ethyl-3-methylimidazolium based ionic liquids

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Received February 8, 2012; accepted May 30, 2012; published online July 17, 2012

In order to examine the chemical form of uranyl species in 1-ethyl-3-methylimidazolium (EMI) based ionic liquids, UV-visible absorption spectra of solutions prepared by dissolving $[EMI]_2[UO_2Cl_4]$ into a mixture of EMICl and $EMIBF_4$ (50:50 mol%) were measured. As a result, it was confirmed that uranyl species in the mixture of EMICl and $EMIBF_4$ existed as $[UO_2Cl_4]^{2-}$. Cyclic voltammograms (CVs) of $[UO_2Cl_4]^{2-}$ in the mixture were measured at 25 °C using a Pt working electrode, a Pt wire counter electrode, and an Ag/Ag^+ reference electrode (0.01 M $AgNO_3$, 0.1 M tetrabutylammonium perchlorate in acetonitrile) in a glove box under an Ar atmosphere. Peaks corresponding to one redox couple were observed around –1.05 V (E_{pc}) and –0.92 V (E_{pa}) vs. ferrocene/ferrocenium ion (Fc/Fc^+). The potential differences between two peaks (ΔE_p) increased from 101 to 152 mV with an increase in the scan rate from 50 to 300 mV s^{-1}, while the $(E_{pc} + E_{pa})/2$ value was constant, –0.989 V vs. Fc/Fc^+ regardless of the scan rate. Furthermore, the diffusion coefficient of $[UO_2Cl_4]^{2-}$ and the standard rate constant were estimated to be 3.7×10^{-8} cm^2 s^{-1} and $(2.7–2.8) \times 10^{-4}$ cm s^{-1} at 25 °C. By using the diffusion coefficient and the standard rate constant, the simulation of CVs was performed based on the reaction, $[UO_2Cl_4]^{2-} + e^- = [UO_2Cl_4]^{3-}$. The simulated CVs were found to be consistent with the experimental ones. From these results, it is concluded that $[UO_2Cl_4]^{2-}$ in the mixture of EMICl and $EMIBF_4$ is reduced to $[UO_2Cl_4]^{3-}$ quasi-reversibly at –0.989 V vs. Fc/Fc^+.

uranyl chloride, ionic liquids, electrochemistry, cyclic voltammetry

1 Introduction

Ionic liquids (ILs) have drawn attention as environmentally benign media, because of their attractive properties such as thermal stability, nonflammability, high ionic conductivity, and wide electrochemical potential windows [1–3]. In the nuclear industry field, it has been also proposed that ILs should be applied as media for reprocessing of spent nuclear fuels and treatments of radioactive wastes contaminated with uranium [4–7]. From such backgrounds, structures [8–23] and electrochemical reactions [24–31] of uranyl species in ILs, and the extraction behavior of uranyl species from acidic aqueous solutions to IL phase [32–38] have been studied widely.

We have also investigated electrochemical behavior of UO_2^{2+} in 1-butyl-3-methylimidazolium based ILs such as BMICl, $BMIBF_4$, and BMINfO (NfO = nonafluorobutanesulfonate) by using cyclic voltammetry to examine applicability of ILs as alternative media to the conventional molten salts in the pyro-reprocessing process [39]. As a result, it was found that the electrochemical reaction of UO_2^{2+} in BMICl was almost reversible and those in $BMIBF_4$ and BMINfO were irreversible, that the UO_2^{2+} species in BMINfO are reduced to U(IV) via U(V) and/or directly to

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U(IV), and that the electrolytic reduction of UO_2^{2+} in BMINfO at −1.0 V vs. Ag/AgCl produces the uranium compounds such as UO_2 and uranium oxychlorides on a carbon cathode electrode. Furthermore, we have examined the chemical forms of uranyl species in BMICl solutions dissolved $Cs_2UO_2Cl_4$ or $UO_2Cl_2 \cdot nH_2O$ and their electrochemical behavior at 80 ± 1 ℃ using cyclic voltammetry [40]. We found that the uranyl species in BMICl exists as $[UO_2Cl_4]^{2-}$ and is reduced to $[UO_2Cl_4]^{3-}$ quasi-reversibly. On the other hand, Giridhar *et al.* have reported that the uranyl species in solutions prepared by dissolving uranyl nitrate into BMICl are reduced to UO_2 through an irreversible single step two-electron transfer [27, 28]. This is different from our result. However, Sornein *et al.* have examined the electrochemical behavior of $[UO_2Cl_4]^{2-}$ in $[BMI][Tf_2N]$ (Tf_2N = bis(trifluoromethylsulfonyl)imide) [25, 31], and reported that the reduction of $[UO_2Cl_4]^{2-}$ proceeded through the ECE mechanism and that under the presence of a large excess of Cl^- ions $[UO_2Cl_4]^{2-}$ is reduced to $[UO_2Cl_4]^{3-}$ quasi-reversibly without any successive chemical reactions. This is consistent with our result.

From the above information, it is suggested that the electrochemical behavior of $[UO_2Cl_4]^{2-}$ species is strongly affected by the anionic components in the BMI^+ based ILs and that the $[UO_2Cl_4]^{2-}$ species in the IL solutions containing a large excess of Cl^- ions is reduced to $[UO_2Cl_4]^{3-}$ without depending on kinds of cationic components of ILs. More recently, in order to examine the validity of our suggestion, we carried out spectroelectrochemical experiments using sample solutions prepared by dissolving $[EMI]_2[UO_2Cl_4]$ (5.48×10^{-2} M, M = mold m^{-3}, EMI = 1-ethyl-3-methylimidazolium) into the mixture of EMICl (M.P. = 89 °C) and $EMIBF_4$ (M.P. = 15 °C) with a molar ratio (%) = 50:50 (abbreviated as $EMIBF_4$/Cl, $[Cl^-] = [BF_4^-] = 3.54 \times 10^{-1}$ M) at 25 °C [41], because this mixture is liquid at room temperature and the molar ratio of Cl^- to UO_2^{2+} in the sample solution is 10.5. As a result, it was confirmed that the $[UO_2Cl_4]^{2-}$ species is reduced to $[UO_2Cl_4]^{3-}$ at −0.996 V vs. ferrocene/ferricenium (Fc/Fc^+), and clarified that the resulting $[UO_2Cl_4]^{3-}$ species is kinetically stable (the disproportionation reaction of $[UO_2Cl_4]^{3-}$ is slow) and shows the characteristic absorption bands of uranyl(V) species at 406, 630, and 770 nm [41].

However, the details of electrochemical reaction of $[UO_2Cl_4]^{2-}$ in $EMIBF_4$/Cl have not been reported. In this paper, we introduce the results of studies on the chemical form and electrochemical properties of uranyl species in $EMIBF_4$/Cl dissolved $[EMI]_2[UO_2Cl_4]$ in more detail.

2 Experimental section

2.1 Materials and chemicals

1-Ethyl-3-methylimidazolium chloride and $EMIBF_4$ were commercially available from Kanto Chemical Co., Inc. The former was repeatedly (at least 4 times) treated with activated charcoal in acetonitrile, followed by filtration and vacuum evaporation, and the latter was used without further purification. The $[EMI]_2[UO_2Cl_4]$ was prepared by the similar method reported previously [26].

2.2 Spectrophotometric and electrochemical measurements

UV-visible absorption spectra of solutions prepared by dissolving $[EMI]_2[UO_2Cl_4]$ into $EMIBF_4$/Cl were measured by using a SHIMADZU UV-3150 spectrophotometer. Cyclic voltammetric (CV) measurements of sample solutions were carried out at 25 °C under a dry Ar atmosphere using BAS ALS660B. A conventional three-electrode system was utilized, i.e., a Pt disc working electrode (surface area (S): 0.020 cm^2), a Pt wire counter electrode, and an Ag/Ag^+ reference electrode (0.01 M $AgNO_3$, 0.1 M tetra-*n*-butylammonium perchlorate in acetonitrile) connected to the sample solution through a glass frit filled with the solvent ionic liquid. The Fc/Fc^+ couple was used as the reference redox system [42]. All potentials reported here are vs. Fc/Fc^+. Dissolved O_2 in the sample solutions was removed by passing Ar gas through for at least 10 min before starting the CV measurements. The ohmic drop in the CV experiment was compensated by subtracting the cyclic voltammogram of the blank $EMIBF_4$/Cl solution from that of $[UO_2Cl_4]^{2-}$ in the same solvent.

3 Results and discussion

3.1 UV-visible absorption spectra

The UV-vis absorption spectrum of $EMIBF_4$/Cl solution ($[Cl^-] = [BF_4^-] = 3.54 \times 10^{-1}$ M, $[Cl^-]/[UO_2^{2+}] = 10.5$) dissolved $[EMI]_2[UO_2Cl_4]$ (5.48×10^{-2} M) is shown in Figure 1, and found to have a remarkable vibrational fine structure. This phenomenon is similar to that of $[UO_2Cl_4]^{2-}$ in $AlCl_3$/EMIC [9], $BMITf_2N$, $MeBu_3NTf_2N$, and C_4minTf_2N (Tf_2N = bis-(trifluoromethanesulfonyl)imide, $MeBu_3N$ = tri-*n*-butylmethylammonium, C_4min = 1-hexyl-3-methylimidazolium) [8, 17]. The molar absorption coefficient (ε) at 429 nm is 12.0 M^{-1} cm^{-1}, and almost the same as those reported by Sornein *et al.* [25] and Nockemann *et al.* [17]. These results indicate that the uranyl species in $EMIBF_4$/Cl solution ($[Cl^-]/[UO_2^{2+}] = 10.5$) dissolved $[EMI]_2[UO_2Cl_4]$ exist as $[UO_2Cl_4]^{2-}$, and are consistent with our previous result that the uranyl species in solutions prepared by dissolving $Cs_2UO_2Cl_4$ or $UO_2Cl_2 \cdot nH_2O$ into BMICl is present as $[UO_2Cl_4]^{4-}$ [41]. In addition, this suggests that in the IL solutions of $[Cl^-] >> [UO_2^{2+}]$ the uranyl species exist as $[UO_2Cl_4]^{4-}$ regardless of kinds of ILs.

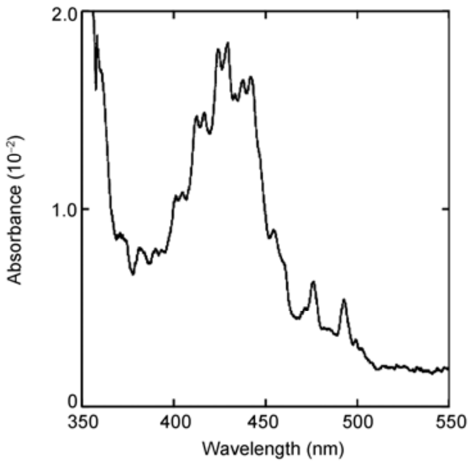

Figure 1 UV-visible absorption spectrum of the solution prepared by dissolving $[EMI]_2[UO_2Cl_4]$ (5.48×10^{-2} M) into $EMIBF_4/Cl$. $[Cl^-]/[UO_2^{2+}] = 10.5$. Temp. = 25 ℃.

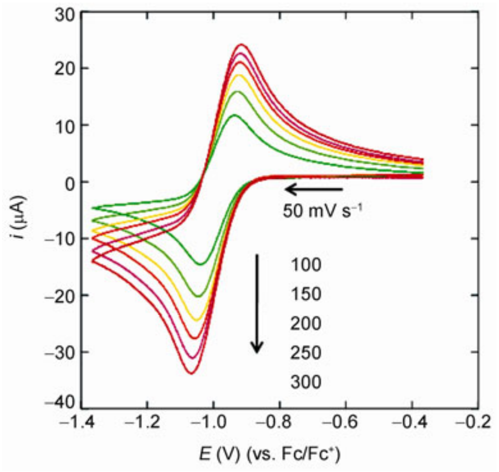

Figure 2 Cyclic voltammograms of the solutions prepared by dissolving $[EMI]_2[UO_2Cl_4]$ (6.06×10^{-2} M) into $EMIBF_4/Cl$ measured at different scan rates (v = 50–300 mV s^{-1}). $[Cl^-]/[UO_2^{2+}] = 9.8$. Temp. = 25 °C. Initial scan direction: cathodic.

3.2 CV measurements

Cyclic voltammograms of the sample solutions ($[Cl^-]/[UO_2^{2+}] = 9.8$) prepared by dissolving $[EMI]_2[UO_2Cl_4]$ (6.06×10^{-2} M) into $EMIBF_4/Cl$ were measured at various scan rates (v) in the rage of 50 to 300 mV s^{-1} at 25 °C. The result is shown in Figure 2. As seen from this figure, two peaks corresponding to one redox couple were observed around −1.05 (E_{pc}) and −0.92 V (E_{pa}). The electrochemical data are summarized in Table 1. The potential differences between two peaks (ΔE_p) increase from 101 to 152 mV with an increase in v, while the values of $(E_{pc} + E_{pa})/2$ are almost constant at −0.989 ± 0.002 V regardless of v. From these results, it is suggested that $[UO_2Cl_4]^{2-}$ in $EMIBF_4/Cl$ is reduced to $[UO_2Cl_4]^{3-}$ quasi-reversibly and that the formal redox potential (E°) is −0.989 V in the present system.

$$[UO_2Cl_4]^{2-} + e^- = [UO_2Cl_4]^{3-} \quad E^{\circ} = -0.989 \text{ V} \tag{1}$$

This is consistent with our previous result that the $[UO_2Cl_4]^{2-}$ species in BMICl are reduced to $[UO_2Cl_4]^{3-}$ quasi-reversibly [40] and the results of Sornein *et al.* that the $[UO_2Cl_4]^{2-}$ species in $BMITf_2N$ containing BMICl ($[Cl^-]/[UO_2^{2+}] > 8.8$) is reduced to $[UO_2Cl_4]^{3-}$ [25, 31]. Furthermore, our recent spectroelectrochemical study clarified that the reduction product ($[UO_2Cl_4]^{3-}$) is kinetically stable (the disproportionation reaction of $[UO_2Cl_4]^{3-}$ is slow) in the $EMIBF_4/Cl$ solution ($[Cl^-]/[UO_2^{2+}] = 9.8$) [41]. On the other hand, Sornein *et al.* reported that the $[UO_2Cl_4]^{2-}$ species in $BMITf_2N$ are reduced to U(IV) through ECE mechanism [31] and Giridhar *et al.* proposed that uranyl nirate in BMICl is reduced to U(IV) via the single step two-electron transfer [28]. These results suggest that the reduction reactions of uranyl species in ILs are strongly affected by the coordination of anionic components of solvent ILs to the equatorial plain of uranyl moiety without depending on the cationic components of ILs.

In order to evaluate reversibility of the reaction (1), the diffusion coefficient (D) of $[UO_2Cl_4]^{2-}$ and the standard rate constant (k^0) were estimated. The D values were estimated by using eq. (2) held for the reversible redox reaction systems at 25 °C.

$$i_p = 269 S n^{3/2} C D^{1/2} v^{1/2} \tag{2}$$

where i_p, n, D, and C are the peak current (A), the electron stoichiometry, the diffusion coefficient of oxidized or reduced species ($cm^2\ s^{-1}$), the concentration of oxidized or reduced species (M) respectively [43]. A plot of i_p values vs. $v^{1/2}$ based on the data in Table 1 is shown in Figure 3, from which a good linear relationship is found. From the slope of

Table 1 Cyclic voltammetric data for solution prepared by dissolving $[EMI]_2[UO_2Cl_4]$ into $EMIBF_4/Cl$, $[UO_2^{2+}] = 6.06 \times 10^{-2}$ M and $[Cl^-]/[UO_2^{2+}] = 9.8$

v (mV s^{-1})	E_{pc} (V)	E_{pa} (V)	ΔE_p (V)	i_{pc} (μA)	i_{pa} (μA)	$(E_{pc}+E_{pa})/2$ (V)
50	−1.038	−0.937	0.101	−14.58	11.71	−0.988
100	−1.045	−0.929	0.116	−20.21	15.94	−0.987
150	−1.051	−0.923	0.128	−24.38	18.81	−0.987
200	−1.056	−0.921	0.135	−27.61	21.06	−0.989
250	−1.064	−0.919	0.145	−31.00	22.62	−0.992
300	−1.067	−0.915	0.152	−33.77	24.20	−0.991

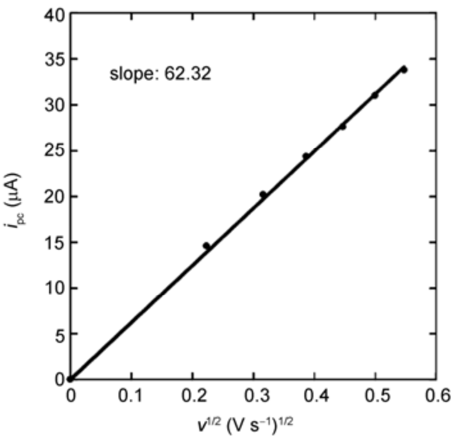

Figure 3 A plot of i_{pc} vs. $v^{1/2}$ for the cyclic voltammograms shown in Figure 2.

this plot, the D value of $[UO_2Cl_4]^{2-}$ was estimated to be 3.7 × 10^{-8} cm^2 s^{-1} at 25 °C, which is comparable to that for uranyl species in BMICl reported by Giridhar *et al.*, 1.69 × 10^{-8} cm^2 s^{-1} at 100 °C [28] and our previous data (7.0 × 10^{-8} cm^2 s^{-1} at 80 °C) obtained in the BMICl solution dissolved $Cs_2UO_2Cl_4$ [40]. The k^0 values were also estimated by Nicholson's equation (eq. (5)) based on the assumption that the diffusion coefficients of oxidized (D_O) and reduced species (D_R) are equal [44, 45],

$$\psi = k^0/\{D\pi(nF/RT)v\}^{1/2} \tag{5}$$

where ψ and F are the kinetic parameter defined by Nicholson and the Faraday constant (96486 C mol^{-1}). Based on Nicholson' paper [44], the ψ values are evaluated as 0.59 and 0.23 at 50 and 300 mV s^{-1}, respectively under the conditions of Temp. = 25 °C and the transfer coefficient (α) = 0.5, because the ΔE_p values at each scan rate are 101 and 152 mV as listed in Table 1. Thus, the k^0 values of the electrochemical reaction (1) were estimated to be 2.8 × 10^{-4} and 2.7 × 10^{-4} cm s^{-1} for v = 50 and 300 mV s^{-1}, respectively by using n = 1 and D = 3.7 × 10^{-8} cm^2 s^{-1} in eq. (5). The k^0 value is related to the reversibility factor (Λ) for electrochemical reactions as follows [43]:

$$\Lambda = k^0/(DnFv/RT)^{1/2} \tag{6}$$

$$\text{Reversible system: } \Lambda > 15$$

$$\text{Quasi-reversible system: } 15 > \Lambda > 10^{-2(1+\alpha)}$$

$$\text{Irreversible system: } 10^{-2(1+\alpha)} > \Lambda$$

If the relation of $D_O = D_R$ = 3.7 × 10^{-8} cm^2 s^{-1} holds in the present electrochemical reaction (1), the equation of Λ is expressed as follows:

$$\Lambda = 8.3 \times 10^2 k^0/v^{1/2} \tag{7}$$

Assuming that the α value is 0.5, the following relationships for k^0 value are derived in the range of v = 50–300 mV s^{-1}.

$$\text{Reversible system: } k^0 > (4.0\text{–}9.9) \times 10^{-3}$$

$$\text{Quasi-reversible system: } (4.0\text{–}9.9) \times 10^{-3}$$

$$> k^0 > (2.7\text{–}6.6) \times 10^{-7}$$

$$\text{Irreversible system: } (2.7\text{–}6.7) \times 10^{-7} > k^0$$

Based on this classification, the electrochemical reaction (1) is regarded as the quasi-reversible reaction under the present experimental conditions, because the estimated k^0 values ((2.7–2.8) × 10^{-3} cm s^{-1}) are in the range (4.0–9.9) × 10^{-3} > k^0 > (2.7–6.6) × 10^{-7}.

3.3 Simulation of cyclic voltammograms

In order to confirm the validity of the estimated D and k^0 values, we performed simulation of cyclic voltamogramms at v = 50 and 300 mV s^{-1} using the software equipped with BAS electrochemical analyzer ALS model 660B. Parameters and conditions used in simulation are as follows: the formal redox potential (E^o) = –0.989 V, D = 3.7 × 10^{-8} cm^2

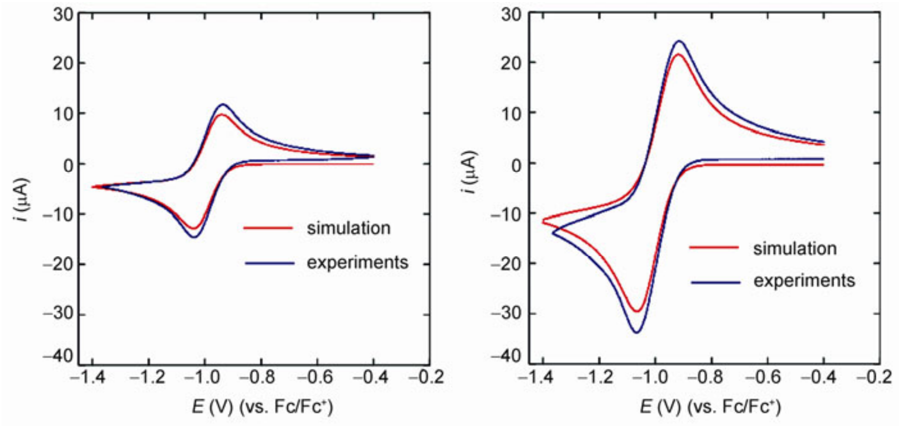

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Figure 4 Comparison of the experimental cyclic voltammogram with the simulated one of the solutions prepared by dissolving $[EMI]_2[UO_2Cl_4]$ (6.06 × 10^{-2} M) into $EMIBF_4$/Cl. (a) scan rate = 50 mV s^{-1}; (b) scan rate = 300 mV s^{-1}.

s^{-1}, $k^0 = 2.8 \times 10^{-4}$ cm s^{-1} at 50 mV s^{-1} and 2.7×10^{-4} cm s^{-1} at 300 mV s^{-1}, Temp. = 25 °C, $[UO_2Cl_4^{2-}] = 6.6 \times 10^{-2}$ M, $S = 0.020$ cm^2, and mechanism: $[UO_2Cl_4]^{2-} + e^- = [UO_2CL_4]^{3-}$ (E mechanism). The results are shown in Figure 4. The simulated cyclic voltammograms are found to be in fair agreement with the experimental ones. The ΔE_p values in the simulated cyclic voltammograms at 50 and 300 mV s^{-1} are 0.099 and 0.146 V, respectively, which are almost consistent with the experimental values (0.101 and 0.152 V) shown in Table 1.

From these results, it is concluded that the $[UO_2Cl_4]^{2-}$ species in EMIBF$_4$/Cl is reduced to $[UO_2Cl_4]^{3-}$ quasi-reversibly and that the estimated D and k^0 values are reasonable.

4 Conclusion

It was confirmed that the uranyl species in solutions prepared by dissolving $[EMI]_2[UO_2Cl_4]$ into EMIBF$_4$/Cl exist as $[UO_2Cl_4]^{2-}$, and that this species is reduced quasi-reversibly to $[UO_2Cl_4]^{3-}$ at −0.989 ± 0.002 V vs. Fc/Fc$^+$. Moreover, from the results of studies of ours and other groups, it is proposed that the electrochemical behavior of $[UO_2Cl_4]^{2-}$ species is strongly affected by the anionic components of solvent ILs and that the $[UO_2Cl_4]^{2-}$ species in the IL solutions containing a large excess of Cl$^-$ ions are reduced to $[UO_2Cl_4]^{3-}$ regardless of kinds of ILs.

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