Behavior of UO₂ in a Room-Temperature Ionic Liquid in the Presence of AlCl₃

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Abstract—A study was made of interaction between $AlCl_3$ and room-temperature ionic liquid (RTIL) $[C_8H_{15}N_2][N(SO_2CF_3)_2]$, or BuEtIm— Tf_2N , and of anodic dissolution in RTIL of UO₂ and of a simulated oxide fuel at 297–302 K, depending on the $AlCl_3$ concentration. It was shown that anodic dissolution of UO_2 pellets and a UO_2 —Al mixture in RTIL yields soluble uranium species. Potentiostatic electrolysis of the resulting solutions can yield uranium compounds at the cathode, though with low current efficiencies. The role of $AlCl_3$ in these processes was suggested. A heterophase reaction between UO_2 and $AlCl_3$ was studied, depending on the content of $AlCl_3$ in solution. It was found that the exchange reaction products, soluble uranium species, are accumulated in solution only at the molar ratio $AlCl_3/Tf_2N > 1$.

Implementation of both pyrochemical and conventional aqueous methods of nuclear material processing involves certain problems. These include high operation costs, high corrosivity of structural materials, abundant waste, risk of accidents, etc.

Low-temperature solvents such as room-temperature ionic liquids (RTILs) eliminate or, at least, significantly reduce some of the above-mentioned drawbacks. It is known [1–9] that RTILs are incombustible and virtually nonvolatile at process temperatures of up to 573 K; they exceed aqueous media in radiation resistance and exhibit a high selectivity with respect to the components being separated.

It was of interest to study separation and purification of nuclear materials using such new process media as room-temperature ionic liquids, in particular, to study the possibility of utilization of uranium from the pressed mixture of 90 wt % Al with 10 wt % UO₂, simulating the irradiated oxide fuel. To this end, we studied interaction of AlCl₃ and anodic dissolution of UO₂ and of the pressed Al–UO₂ mixture, as well as the exchange reaction between UO₂ and AlCl₃ in an RTIL of the composition $[C_8H_{15}N_2][N(SO_2CF_3)_2]$, or BuEtIm–Tf₂N, at 297–302 K, depending on the AlCl₃ concentration.

EXPERIMENTAL

We studied the chemical and electrochemical behavior of UO_2 and $Al-UO_2$ mixture in BuEtIm-NTf₂

RTIL by linear and cyclic voltammetry and zerocurrent chronopotentiometry. Also, we carried out electrolysis of ionic liquids of different compositions, followed by the chemical and X-ray phase analyses of the solid and liquid phases.

All manipulations, including assembling the electrochemical cells, were carried out in a dry glove box in an argon atmosphere. Argon was permanently freed from oxygen-containing impurities by forced circulation through a column packed with metallic Zr chips and heated to 1000 K. Argon circulation was effected by a membrane pump placed directly inside the glove box.

As solvent we used RTIL of the composition BuEtIm–Tf₂N, synthesized at the Los Alamos National Laboratory (the United States). Before use, the RTIL was additionally freed from oxygen-containing impurities by keeping at a residual pressure of 10^{-3} atm for 12 h.

Electrochemical studies were carried out in a quartz cell with a ground-down cover, equipped with two pipes connecting the cell to an additional gas-purification system. The cell was placed into a stainless-steel beaker hermetically built into the glove box bottom, which also constituted the external part of the temperature-control system.

The electrolyte under study was placed into a glass container. As working electrode served a face elec-



Fig. 1. Cyclic voltammogram of BuEtIm–NTf₂ RTIL with AlCl₃ addition. Potential sweep range from -4.0 to +4.0 V. Sweep rate 0.2 V s⁻¹. Temperature 302 K. Working electrode tungsten; reference and counter electrodes, glassy carbon. AlCl₃ concentration, mol %: (*1*) 0, (*2*) 38, and (*3*) 61.

trode made of VRN metallic tungsten or of SU-2000 glassy carbon, both with and without fixed surface area. As reference electrode served an Al³⁺/Al system placed into a capsule with a porous diaphragm, filled with BuEtIm-Tf₂N RTIL with a fixed AlCl₃ concentration. An alternative reference electrode was an SU-2000 glassy carbon rod immersed directly in the melt under study. As counter electrode served an SU-2000 glassy carbon rod, a VRN tungsten rod, or a graphite basket with holes, suspended on a molybdenum hanger. A UO₂ pellet or an Al–UO₂ mixture was placed into the basket and used, in a number of cases, as anode. The atmosphere inside the cell was additionally subjected to closed-loop treatment, via a zirconium gas-purification system, using a Zalimp PP-10-5A peristaltic pump. The AlCl₃ concentration in the electrolyte was varied by dropping the required weighed portions of AlCl₃ via a sluice without changing the gas phase compositions.

AlCl₃ was prepared in a special test tube under a purified Ar atmosphere, by slowly introducing metallic Al into molten $PbCl_2$. The AlCl₃ sublimates were condensed in the upper, specially cooled, part of the cell. The resulting product was transferred in a dry box. Prior to experiments, AlCl₃ was subjected to double distillation.

Electrochemical studies were carried out using a standard PI-50-1 potentiometer with a PR-8 programmer, by recording electrochemical responses of the system with an S9-8 digital storage oscillograph connected to a PC. The potential sweep rate was varied from 0.05 to 10 V s⁻¹. The experiments were run at 298–308 K.

RESULTS AND DISCUSSION

Figure 1 presents cyclic voltammograms of the BuEtIm-NTf₂ RTIL with and without AlCl₃ addition, recorded at 302 K in an inert gas atmosphere. The cyclic voltammogram of the RTIL without AlCl₃ (curve 1) exhibits an increase in the current at the potential of -2.1 V in the cathodic branch and a weakly manifested wave at +2.3 V in the anodic branch relative to the glassy-carbon reference electrode. Upon introduction of AlCl₃, the run of the voltammogram regularly changed (curve 2). In the anodic branch of the cyclic voltammogram, a wave appeared at 1.7 V, probably due to oxidation of the chloride ions. A similar pattern was observed by Store et al. [10]. Increase in the AlCl₃ concentration (curve 3) leads to a regular increase in the limiting currents corresponding to discharge of the chloride ions. This suggests that the appearance of the chloride ions in solution is due to AlCl₃ occurring in the RTIL. Gaseous chlorine, a strong oxidant, released at the anode and in the bulk of RTIL was responsible for a change in the color of the ionic liquid and its partial degradation.

The Al^{3+} cations exhibit a complex behavior in the ionic liquid. Supposedly, $AlCl_3$, a strong Lewis acceptor, reacts with the Tf_2N^- anion, forming a heteroligand complex, in which the coordination sphere of Al, along with the three chloride ions, contains one of the oxygen atoms from the SO₂ group of the Tf_2N^- anion. This was the case for GaCl₃ in RTIL, as demonstrated by our spectroscopic and voltammetric studies [11–14]. Close chemical properties of gallium and aluminum compounds suggest their similar behavior in identical solutions.

Figure 2 (curve 1) shows a cyclic voltammogram recorded upon dissolution of the UO_2 pellet in the BuEtIm–NTf₂ + AlCl₃ solution. After anodic dissolution (uranium concentration in solution after dissolution 1.7 mol %), peaks were observed in the anodic branch of the curve at -0.997 and 0.914 V. Formation of these waves is evidently due to the appearance of soluble uranium species participating in the electrochemical process. It is known [4, 15] that uranium oxide species are converted into oxygen-free species upon introducing AlCl₃ into an RTIL. Probably, in our case oxygen-free uranium species were also present in solution.

The potential vs. time plots recorded after brief polarization of the cathode in the region of possible deposition of uranium compounds (E > -1.0 V) exhibit a plateau in the potential decay curves, which suggests formation of a solid product containing,



Fig. 2. Cyclic voltammogram of the BuEtIm–NTf₂ RTIL with AlCl₃ and UO₂ additions. Potential sweep range from -6.0 to +6.0 V. Sweep rate 0.2 V s⁻¹. Temperature 302 K. Concentrations, mol %: AlCl₃ 10 and uranium 1.7. Working electrode tungsten; reference and counter electrodes, glassy carbon. (1) Voltammogram recorded after anodic dissolution of the UO₂ pellet (m = 2.00 g); uranium concentration 1.7 mol %, and (2) voltammogram recorded after anodic dissolution of the pressed Al–UO₂ mixture (m = 2.67 g); uranium concentration 1.8 mol %.



Fig. 3. Potential vs. time plot recorded after brief polarization of the tungsten cathode in RTIL. Temperature 302 K. Working electrode tungsten; reference electrode AI^{3+}/AI ; and counter electrode glassy carbon. RTIL BuEtIm–NTf₂. Concentrations, mol %: AICl₃ 30 and uranium 2.3. Polarization potential -4.1 V; polarization time 120 s.

evidently, uranium compounds or uranium. In the case of the RTIL with $AlCl_3$ without anodic dissolution of UO_2 , there was no plateau. Chemical analysis of the solution after anodic dissolution of UO_2 confirmed the presence in BuEtIm–NTf₂ + $AlCl_3$ of soluble uranium species (1–3 mol %). Potentiostatic electrolysis of the solution at various deposition potentials of uranium showed a low current efficiency (<5%) of the deposition. A typical X-ray diffraction pattern of the cathodic product shows its amorphous structure, which prevented its X-ray phase analysis. At the same time, chemical analysis of the cathodic product revealed the presence of a uranium compound.

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In the case of anodic dissolution of the pellets (containing 90 wt % Al and 10 wt % UO₂), simulating the oxide nuclear fuel, in the potentiostatic electrolysis mode (Fig. 2, curve 2), the voltammogram was virtually identical to that recorded with the UO₂ pellet under identical conditions (Fig. 2, curve 1). Prolonged (>24 h) potentiostaic electrolysis at a potential of -6 V vs. glassy carbon reference electrode yielded a cathodic deposit, the current efficiency being no greater than 5% either. Chemical analysis of the deposit revealed 2.75 wt % U, the final concentration of uranium in solution being 0.013 mol %.

Komarov and Borodina [16] reported on a heterophase reaction between UO₂ and trivalent aluminum in a NaCl-KCl melt. We studied a chemical reaction between UO_2 and $AlCl_3$ in the RTIL over a wide range of AlCl₃ concentrations by voltammetric and spectroscopic methods. We found that, at $AlCl_3/Tf_2N^- < 1$, the voltammograms and spectrograms remained unchanged upon keeping the UO₂ powder and pellet in solution for 72 h. This suggests the lack of chemical reactions between the components, UO₂ and AlCl₃, under the actual conditions. This can be due to formation in solution of a heteroligand complex of aluminum, $AlOCl_3^{2-}$, as mentioned above. The acceptor power of $AlOCl_3^{2-}$ should be much weaker compared to AlCl₄. Indeed, more recent studies showed that soluble uranium species appeared in solution only when the AlCl₃/Tf₂N⁻ molar ratio exceeded unity, i.e., when oxygen-free aluminum species appeared in solution. In this case, soluble uranium species were revealed in the concentration of 0.016 mol % upon 6-h keeping in RTIL.

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