

Supporting Information

Remarkably Enhanced Direct Dissolution of Plutonium Oxide in Task Specific Ionic Liquid: Insights from Electrochemical and Theoretical Investigations

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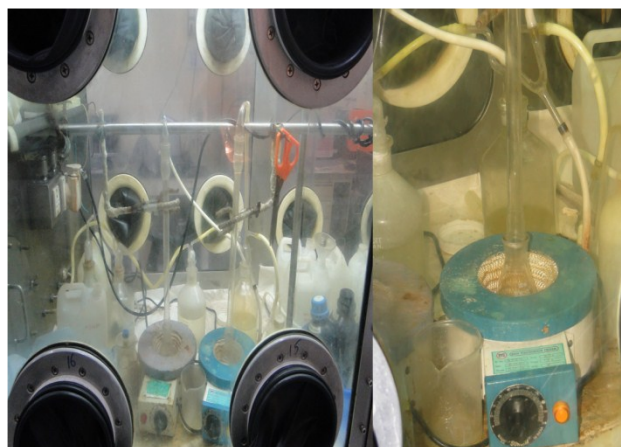
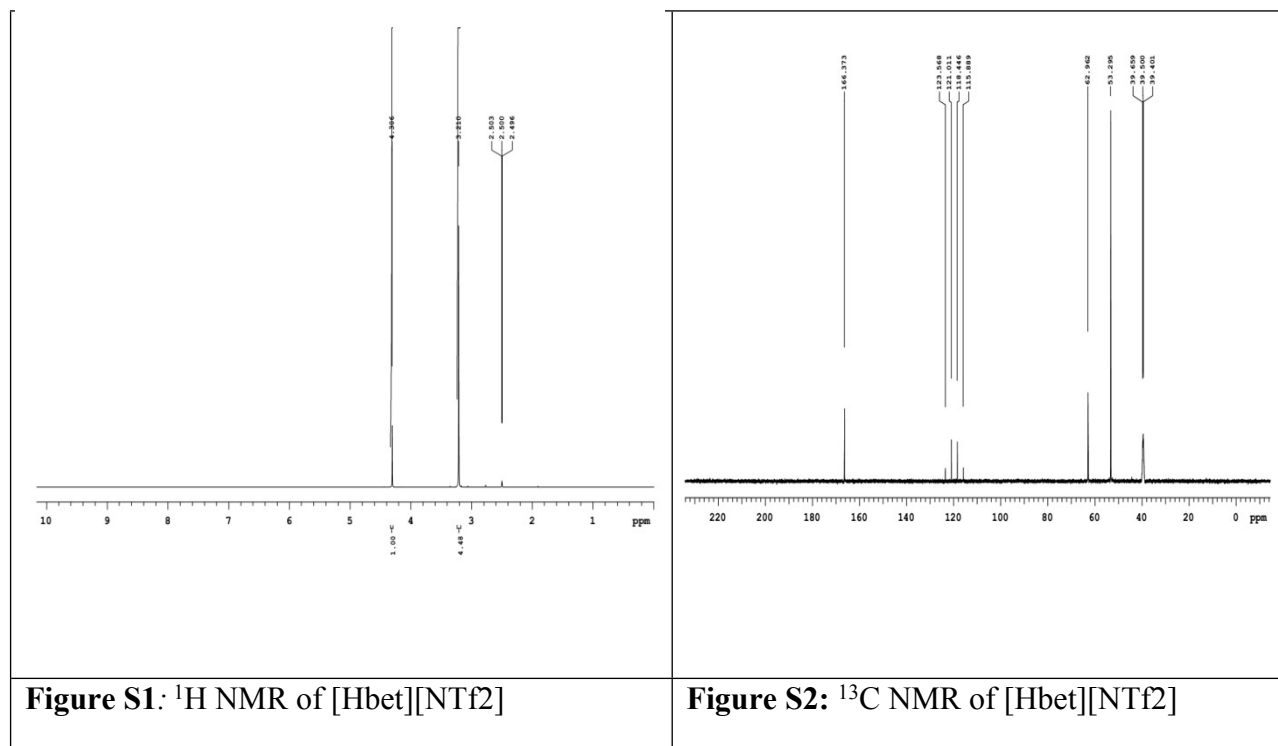
EXPERIMENTAL SECTION

All the chemicals used in this study were used as received. Betaine hydrochloride and lithium bis(trifluoromethanesulfonylimide) were purchased from Sigma Aldrich. [Hbet][NTf2] was prepared by the procedure described elsewhere¹. In brief lithium bis(trifluoromethylsulfonyl)imide (0.05 mol, 14.4 g) was dissolved in 50 mL of H₂O, and an aqueous solution (25 mL) of betaine hydrochloride (0.05 mol, 7.7 g) was added to it under stirring. After 2 h of stirring, the ionic liquid phase was separated, washed with H₂O (3 x 15 mL) to remove any traces of chloride impurities, and finally dried under vacuo to obtain pure [Hbet][NTf2] (Yield 12.3 g, 62%). ¹H NMR (500 MHz, DMSO-d₆): δ 3.21 (s, 9H), 4.31 (s, 2H); ¹³C NMR (125 MHz, DMSO-d₆): δ 53.3, 63.0, 115.9, 118.4, 121.0, 123.6, 166.4. (For information: MilliQ water (resistivity higher than 18.2 M Ω .cm) was used for synthesis. . ¹H and ¹³C NMR spectra were recorded with a 500 MHz Varian NMR spectrometer, and FIDs were processed using MestReNova v1.13 software and are shown in Figure S1 and Figure S2 . The water content in the ionic liquid was found to be insignificant as evident from thermogravimetric studies discussed later. The set up for PuO₂ dissolution is shown in scheme 1. The refluxion process was continued until all the PuO₂ powder got dissolved in RTIL. The aliquot of [Hbet][NTf2] containing plutonium, in the present study, was also equilibrated with 1M HNO₃ to strip the plutonium from the ionic liquid aliquot and the amount of plutonium in nitric acid was estimated by alpha counting. The alpha activity of the aqueous phase, before and after solvent extraction, was measured by alpha spectrometry using PIPS alpha detectors (PIPS Canberra PD-300-16-100AM detector having 300 mm² surface area, 100 μ m active thickness, 16 KeV FWHM at 5.4 MeV energy of alpha particles emitted by ²⁴¹Am). Voltammetric studies of the solutions were recorded using CHI 760D electrochemical workstation in the temperature range 298–351 K. A glassy carbon disk working electrode (area, A = 0.07 cm²) was used as working electrode. Two Pt wires acted as counter and quasi-reference electrodes. Platinum quasi reference electrode was calibrated with respect to the ferrocene/ferrocenium (Fc/Fc⁺) redox couple in ionic liquid and E₀ was observed as = 0.21 V. The internal standard Fc/Fc⁺ was added to ([Hbet][NTf2]) ILs and all the redox potentials are referred against the Fc/Fc⁺ redox couple. All solutions were deoxygenated using high purity argon prior to electrochemical experiments. Each measurement was repeated thrice and the average numerical value of each parameter is quoted for discussion with a relative error < \pm 0.1%. The electrochemical cell had a single leak-

tight compartment and all the electrodes were placed in the same compartment. The cell was kept under argon atmosphere during entire study. The thermal stability of ionic liquid was studied using thermogravimetry- differential scanning calorimeter (TGDSC) model No: DSC-2 and the low temperature phase transition was studied using a differential scanning calorimeter (DSC 823e). Both the instrument was supplied by M/s Mettler Toledo Pvt Ltd, Switzerland. The experiments were carried out at a heating /cooling rate of 5K/min. Reversible run was carried out in DSC, however, only heating run was carried out in TG-DSC. The alpha spectrum of Pu electro-deposited on a polished stainless steel planchette was recorded using a passivated ion-implanted planar silicon detector PIPS Canberra, PD-300-24-100AM, 300 mm² surface area, 100 μ m active thickness, 24 keV FWHM at 5.486 MeV energy of alpha particles emitted by ²⁴¹Am). The electro-deposited alpha source was placed at a distance of about 1 cm from the PIPS detector in a vacuum chamber and pressure inside the chamber was reduced to 10⁻⁶ bar. The detector voltage was applied with a 100 Volt HV-unit (M/s ECIL, India), fixed in a 6-slot NIM Bin (M/s Gyanic Systems, India). The alpha spectrum was recorded by a PC-based 8K-MCA coupled to the PIPS detector through a USB interface. In order to achieve good counting statistics, the spectrum was recorded for a time to accumulate minimum 10,000 counts at the characteristics alpha energies of Pu isotopes. The analyses of peak area at the characteristics alpha energies of ^{238,239,240}Pu were carried out using PCA3 software.

Caution!!

²³⁹Pu is an α -active nuclide with a half-life of 2.4×10^4 years which corresponds to the production of 138×10^6 α -particles/min/mg of Pu. Plutonium is notoriously hazardous when it finds its way into the human body. It should be studied exclusively in actinide laboratory equipped with glove boxes and analytical apparatus for actinide research to avoid any health risk caused by the radiation exposure.



Scheme1: Set up for PuO₂ dissolution inside glove box

Thermograms recorded for the synthesized ([Hbet][NTf₂]) ionic liquid are given in Figure.S1 In Figure S3 , DSC curve showed a glass transition around -56°C as explained in literature². Later at -16.8°C, the process of cold crystallisation occurred and was reflected as exothermic peak in Figure S3 (A). The melting of IL occurred at 28.6°C, which comprised of two unresolved

endothermic peaks merging with each other. In the cooling curve crystallisation of ILs occurred at 4°C, which was reflected as a single sharp peak. The difference in melting and crystallisation temperature might be due to supercooling effect. The weight loss curve in Figure S3 (B) showed two loss processes due to decomposition of IL at 310 °C and 426°C, respectively. Hence IL is predicted to be stable upto temperature of 300°C. The loss processes were reflected as endothermic peak in figure S3(B) in heat flow rate curve. The two merging peaks during melting in Figure S3(A) and two decomposition peaks in TG-curve in FigureS3(B) indicates presence of two moiety in the ILs of which one moiety is less strongly bound and the other is more strongly bound. The less strongly bound part decomposed at 310°C and the more strongly bound decomposes at 426°C.

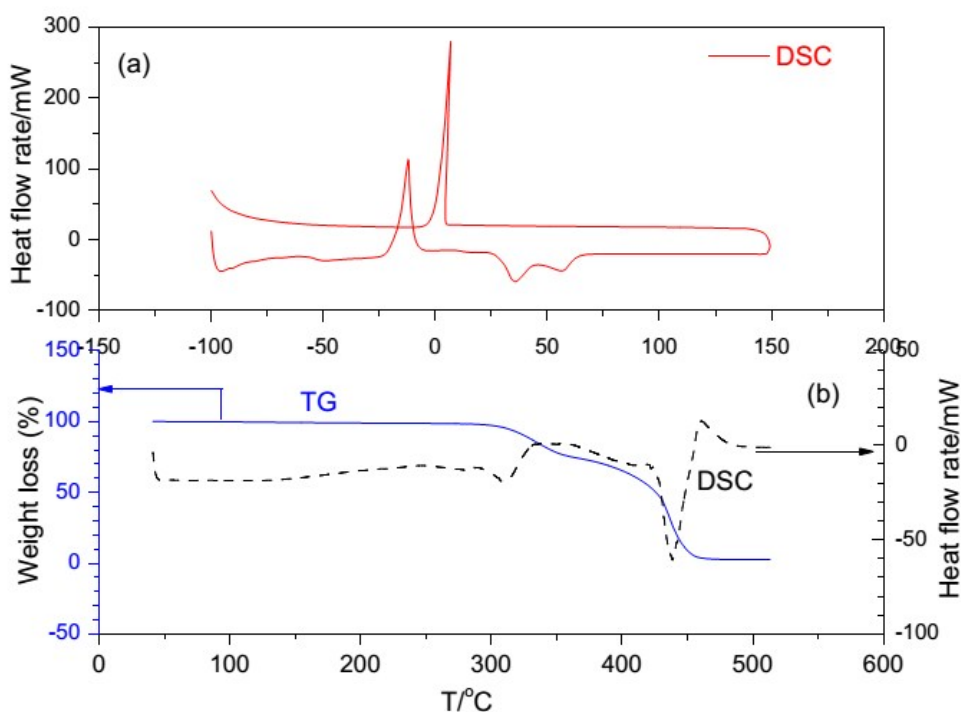


Figure S3: Thermograms recorded for the synthesized ([Hbet][NTf2]) ionic liquid

After complete dissolution of PuO₂ in ionic liquid, UV-Vis spectroscopy was undertaken to see the predominant oxidation state in the resulted solution. Figure S4 presents the UV-Visible spectra of plutonium in [Hbet][NTf2]. The most prominent peak observed at 476 nm in [Hbet][NTf2] was attributed to Pu(IV).

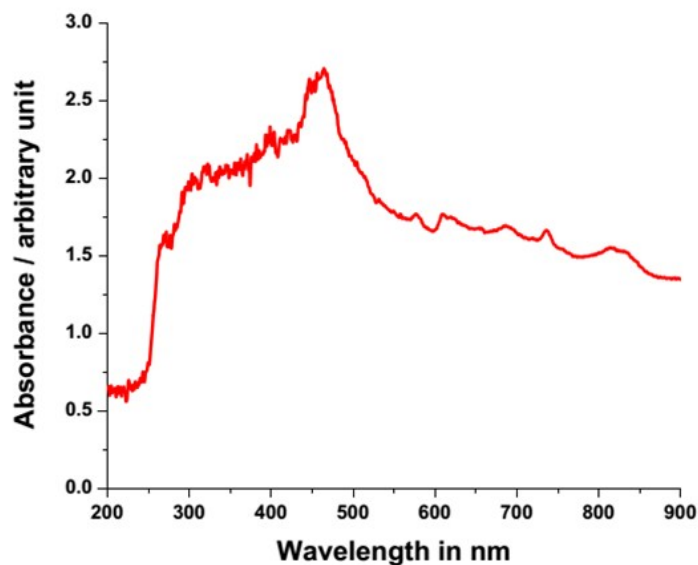


Figure S4: UV-Visible spectra of plutonium directly dissolved in [Hbet][NTf₂]

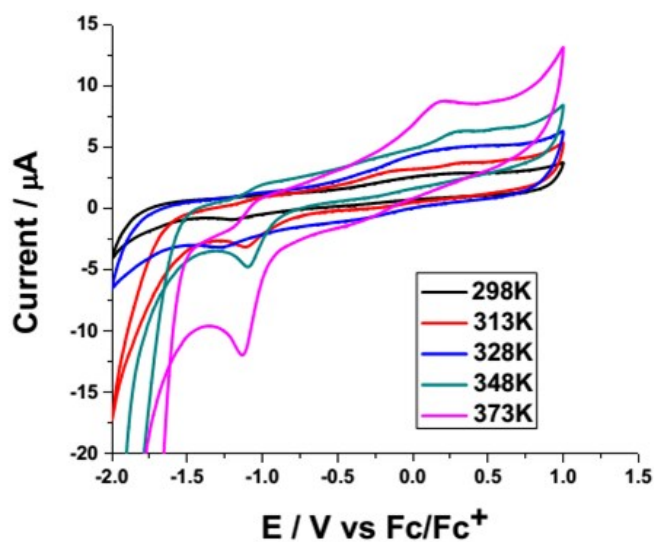
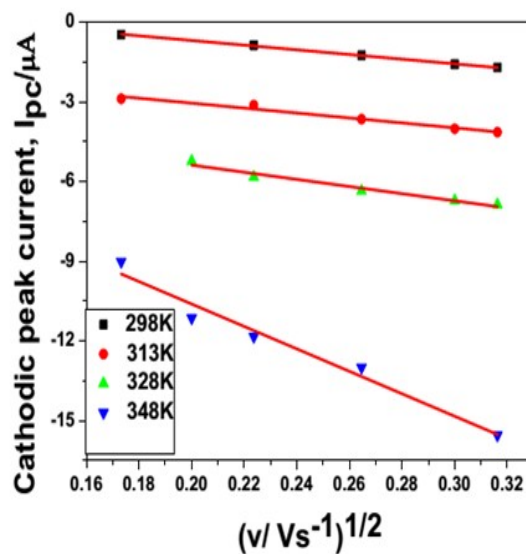


Figure S5: Cyclic voltammograms of 9 mM Pu(IV) in [Hbet][NTf₂] at various temperatures.



FigureS6: The plots of cathodic peak current (I_{pc}) against the square-root of the potential scan rate ($v^{1/2}$) at different temperatures.

Figure S5 shows the cyclic voltammograms of 9 mM Pu(IV) in [Hbet][NTf2] at various temperatures. Temperatures were well controlled and selected as 298 K, 313 K, 328 K, 348 K and 373 K, respectively. For Pu(IV) in [Hbet][NTf2], the current densities increased along with the rise of temperature. This feature is associated with the mass transition caused by the viscosity of [Hbet][NTf2], which depends on temperature closely. Thus, the transport properties of ILs, including conductivity, diffusion coefficient, and charge transfer rate are also temperature-dependent for the variation of viscosity. For [Hbet][NTf2] ionic liquid, its viscosity decreased and the conductivity increased at higher temperature, which would facilitate the diffusion of Pu(IV). The diffusion rate also enhances as the temperature is increased. Both current intensity and peak potential were changed, along with the change of scan rate. The anodic peak potentials were shifted to anodic direction with increase in temperature and the cathodic peak potential also shifted to more anodic direction and the anodic peaks were less sharp than the cathodic ones as the temperature reached 348K. The plots of cathodic peak current densities (I_{pc}) against the square-root of the potential scan rate ($v^{1/2}$) are shown in Figure S6 at different temperatures.

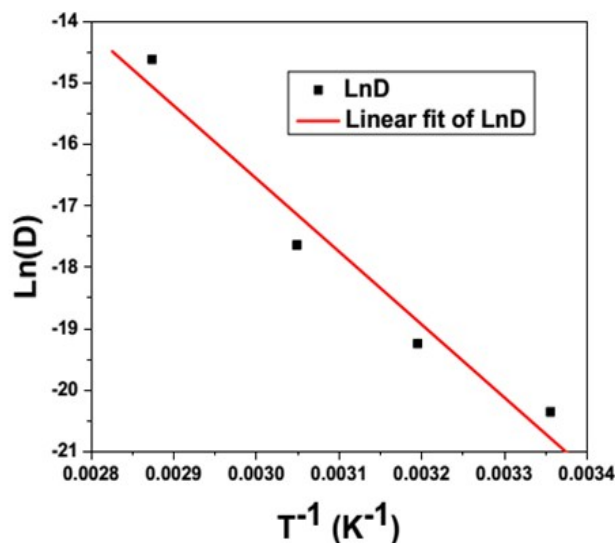


Figure S7: A plot of $\ln D$ versus $1/T$

The linear dependence of I_{pc} on square root of scan rate ($v^{1/2}$), shown in Figure S7 also confirms the reduction of Pu(IV) to Pu(III) in [Hbet][NTf2] ILs is diffusion controlled. A positive correlation of the current intensity with the square root of scan rate was also seen. The cathodic peak current (I_{pc}) and the scan rate for a quasireversible reduction reaction for a soluble-soluble couple are related to each other by equation 1.

$$I_{pc} = 0.496 n F A C D^{1/2} \left(\frac{\alpha n_{\alpha} F v}{RT} \right)^{1/2} \quad (1)$$

where C is the plutonium concentration in mol cm^{-3} , D is the diffusion coefficient in $\text{cm}^2 \text{s}^{-1}$, F is the Faraday constant, n is the number of exchanged electrons, v is the scan rate in Vs^{-1} , α is the charge transfer coefficient, n_{α} is the number of electrons transferred in the rate determining step,

A is the geometric area of electrode and T is the absolute temperature in K. The value of αn_α can be determined from equation 2

$$|E_{pc} - E_{pc/2}| = \frac{1.857RT}{F\alpha n_\alpha} \quad (2)$$

Where, $E_{pc/2}$ is the half-peak potential. The value of αn_α was found at different temperatures for the scan rate of 0.02Vs^{-1} . Substituting the value obtained in Eq. (2), the diffusion coefficient of Pu(IV) in [Hbet][NTf2] was determined at different temperatures and are given in table 1. Since the reduction of tetravalent plutonium is not only controlled by diffusion but also by charge transfer kinetics, the rate constant of charge transfer reaction, k_s can be determined using the equation 3.

$$k_s = 2.18 \left[D(\alpha n_\alpha) \frac{\nu F}{RT} \right]^{1/2} \exp \left[\frac{\alpha^2 n F}{RT} (E_{pc} - E_{pa}) \right] \quad (3)$$

The electrode reaction can be classified as reversible when $k_s \geq 0.3\nu^{1/2} \text{ cm s}^{-1}$, quasi-reversible when $0.3\nu^{1/2} \leq k_s \leq 2.0 \times 10^{-5} \nu^{1/2} \text{ cm s}^{-1}$ and irreversible when $k_s \leq 2.0 \times 10^{-5} \nu^{1/2} \text{ cm s}^{-1}$. The k_s values for the reduction of Pu(IV) to Pu(III) at different temperatures in ionic liquid media are summarized in Table 1. The reduction was found to be quasi reversible as suggested by the k_s values in all the cases. With increase in temperature, the k_s value increased indicating the increase in reversibility and can be attributed to the facilitated electron transfer at electrode–electrolyte interface at high temperatures. k_s values were found to be less in ionic liquid phase as compared to aqueous phase indicating the increase in irreversibility in RTIL which is attributed to the retardation of the electron transfer at electrode – electrolyte interface due to high viscosity.

Table 1:

Temperature (K)	D (cm ² /s)	k _s (cm/s)
298	3.9×10^{-9}	4.6×10^{-4}
313	4.4×10^{-9}	4.8×10^{-4}
328	8.0×10^{-9}	5.0×10^{-4}
348	6.1×10^{-8}	8.0×10^{-4}

The activation energy for the diffusion of the metal ion can be evaluated using Arrhenius equation 4

$$D_0 = A \exp (-E_a/RT) \quad (4)$$

Where A is the pre-exponential factor and E_a is the corresponding activation energy. A plot of $\ln D$ versus $1/T$ gave a straight line as shown in Figure S7 with a slope of $(-E_a/R)$. From the slope, the activation energy for the diffusion of Pu(IV) was found to be 98.3 KJ/mol for [Hbet][NTf2].

This signifies that 98.3 KJ/mol of energy are required for the diffusion of Pu(IV) ion at electrode–electrolyte interphase in [Hbet][NTf₂] medium.

Computational Details

The geometry optimizations and total energy calculations have been performed using the density functional theory (DFT) based electronic structure programs, as implemented in ORCA-4.0³ programs by employing the GGA based Perdew-Burke-Ernzerhof (PBE)⁴ exchange–correlation functionals. Initially all the geometries were optimized by PBE functional in conjunction with the def2-TZVP basis set. For plutonium, segmented all-electron relativistically contracted basis sets (SARC-TZVP) has been employed⁵. Scalar relativistic all-electron calculations have been performed with the ZORA Hamiltonian. The resolution-of identity approximation has also been applied along with the appropriate auxiliary basis sets. The atomic charge distributions between the plutonium ion and betain IL groups have been calculated by the Mulliken population method, as implemented in the ORCA-4.0 programs.

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