

Review Article

Electrochemical Behaviour of Actinides and Fission Products in Room-Temperature Ionic Liquids

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In the recent past, room-temperature ionic liquids (RTILs) are being explored for possible applications in nuclear fuel cycle. RTILs are being studied as an alternative to the diluent, *n*-dodecane (*n*-DD), in aqueous reprocessing and as possible substitute to high-temperature molten salts in nonaqueous reprocessing applications. This paper deals with the current status of the electrochemical research aimed at the recovery of actinides and fission products using room-temperature ionic liquid as medium. The dissolution of actinide and lanthanide oxides in ionic liquid media and the electrochemical behavior of the resultant solutions are discussed in this paper.

1. Introduction

Nuclear reactors employ natural or enriched uranium as the fuel [1]. The spent nuclear fuel discharged from the nuclear reactor is composed of fissile elements such as plutonium and depleted uranium and several other elements formed by fission reaction, known as fission products. The spent nuclear fuel is, therefore, reprocessed to recover these fissile elements for the fabrication of nuclear fuel for future reactors. There are two different technologically viable methods available for reprocessing of spent nuclear fuel. The first one is the aqueous-based, industrially well-established, PUREX (plutonium uranium recovery by extraction) process [2] and the other is nonaqueous-based pyrochemical process [3]. The PUREX process involves the dissolution of spent nuclear fuel in nitric acid medium followed by the selective extraction of uranium and plutonium in a solution of tri-*n*-butylphosphate (TBP) in *n*-dodecane (DD). However, the undesirable limitation of the PUREX process is the chemical and radiolytic degradation of the solvent system and the generation of large volumes of secondary wastes. The flammability of hydrocarbon employed in the PUREX process is also another disadvantage.

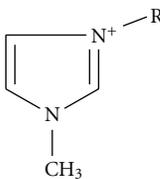
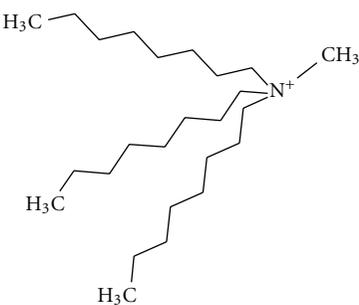
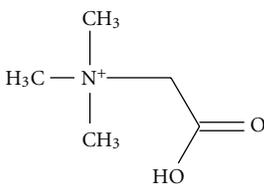
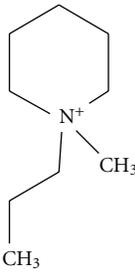
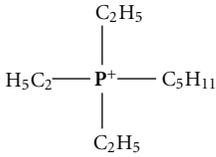
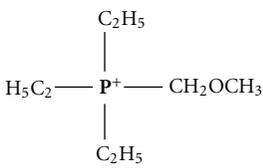
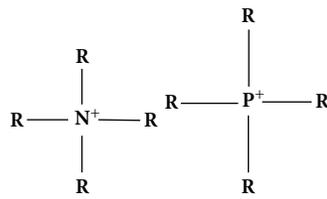
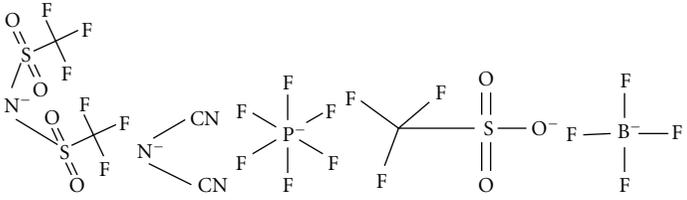
In contrast to this method, the nonaqueous pyrochemical method for reprocessing of spent nuclear fuel has several

advantages, such as minimum waste generation, low criticality concern and feasibility to reprocess the high burn-up, and short cooled fuels. This method exploits the differences in the thermodynamic stabilities of various actinides and fission products for the dissolution of spent nuclear fuel in the inorganic molten salt media followed by the electrochemical recovery of actinides [4]. Usually, the inorganic molten salt is composed of an eutectic of alkali or alkaline earth chloride. Therefore, the processing temperature in this method is invariably above 800 K depending upon the composition of chosen eutectic. In view of this, the pyrochemical method also offers a few challenges with respect to the plant design, requirement of inert atmosphere, high-temperature operation and corrosion problems, and so forth.

2. Room-Temperature Ionic Liquids

Substitution of unsymmetrical organic cation in place of alkali metal cation of the inorganic chloride salt dramatically reduces the melting point of the resultant organic chloride to near ambient temperatures. For instance, the melting temperature of NaCl is 1074 K and that of 1-butyl-3-methylimidazolium chloride (bmimCl) is 343 K. Such organic salts are known as room-temperature ionic liquids (RTILs). According to the most accepted definition, RTILs

TABLE 1: Some of the cations and anions used to form room-temperature ionic liquids.

CATIONS	
	
	
	
	
ANIONS	
	
Cl ⁻ , Br ⁻ ,	

are composed fully of dissociated ions and melt at temperature lower than 373 K [5–7]. Some examples of the cation-anion combinations for making RTILs are shown in Table 1. They have several attractive properties suitable for industrial exploitation such as insignificant vapour pressure, large liquidus range, good electrical conductivity and thermal stability, wide electrochemical window, and amazing ability to dissolve organic and inorganic compounds. In view of this, RTILs are being explored for various applications [7–13].

3. Electrochemical Stability of RTILs

In the recent past, room-temperature ionic liquids are receiving increased attention for possible electrochemical applications in the area of nuclear fuel reprocessing and waste management. For such applications, it is desirable to use an ionic liquid that has good solubility of actinides, excellent thermal and radiation stability, and wide electrochemical window with extended cathodic stability. The

knowledge of electrochemical stability can be derived from the measurement of the electrochemical window of RTIL. The electrochemical window [7, 14, 15] is defined as the potential range in which the ionic liquid does not undergo any oxidation and reduction reactions. Table 2 shows the electrochemical windows of some ionic liquids offering electrochemical window more than 2 V. The abbreviations of the ionic liquids reported are tabulated in Table 3. It is observed that many RTILs offer cathodic stability up to -3.3 V and electrochemical window >4 V. Some RTILs offer window more than 6 V, which is indeed desirable for the electrodeposition of metals such as lithium. Simka et al. [16] reviewed the electrodeposition of highly electropositive metals in ionic liquid media and reported the feasibility of using ionic liquids for such applications. Table 4 summarises the list of metals for which electrodeposition has been reported from RTIL medium [16, 17]. It is observed that several metals ranging from S-block to P-block through the transition metals have been studied. However, the studies related to

TABLE 2: The electrochemical windows of some ionic liquids GC-glassy carbon, VC- vitreous carbon, RDE-rotating disc electrode, and Fc-ferrocene.

Name of the ionic liquid	Cathodic limit, V	Anodic limit, V	Electrochemical window, V (reference electrode)	Working electrode	References
bmimCl	-1.38	0.74	2.12 (Pd)	GC	[18]
	-2.2	2.2	4.4 (Ag)	GC	[19]
bmimBF ₄	-2.2	2.4	4.6 (Ag)	Au	[19]
	-2.4	2.5	4.9 (Ag)	Pt	[19]
	-2.1	+2.5	4.6 (SCE)	—	[8]
bmimPF ₆	-2.50	3.85	6.35 (Pt)	VC RDE	[20]
	-2.1	>5.0	>7.1 (Pt)	W RDE	[20]
bmimNTf ₂	~ -1.9	~2.3	4.2 (Ag)	Pt	[21]
bmimCF ₃ CO ₂	~ -2.0	~0.7	2.7 (SCE)	—	[8]
hmimCl	-0.88	0.75	1.63 (Pd)	GC	[22]
	-1.8	2.4	4.2 (Ag)	GC	[19]
bdmimBF ₄	-2.3	2.3	4.6 (Ag)	Au	[19]
	-2.0	2.3	4.3 (Ag)	Pt	[19]
	-2.4	3.0	5.4 (Ag)	Ta	[19]
HbetNTf ₂	-1.16	1.2	2.4 (Fc/Fc ⁺)	GC	[23]
	-2.91	2.65	5.56 (Fc/Fc ⁺)	GC	[22, 24]
BMPyNTf ₂	~ -3.1	~3.2	6.3 (Pt)	GC	[25]
	-3.0	2.5	5.5 (Ag/Ag ⁺)	GC	[26]
MPPiNTf ₂	-2.71	2.26	4.97 (Fc/Fc ⁺)	GC	[22]
	-3.3	2.3	5.6 (Fc/Fc ⁺)	GC	[27]
P ₂₂₂₅ DCA	~ -3.2	~2.6	5.8 (Ag/Ag ⁺)	Pt	[28]
P ₂₂₂₍₁₀₁₎ DCA	~ -2.5	~3.0	5.5 (Ag/Ag ⁺)	Pt	[28]
N ₂₂₂₍₁₀₁₎ DCA	~ -2.6	~2.4	5.0 (Ag/Ag ⁺)	Pt	[28]
P ₂₂₂₍₂₀₁₎ DCA	~ -2.5	~2.6	5.1 (Ag/Ag ⁺)	Pt	[28]
P ₂₂₂₅ NTf ₂	~ -3.2	~3.0	6.2 (Fc/Fc ⁺)	Pt	[29]
P ₂₂₂₍₁₀₁₎ NTf ₂	~ -3.0	~2.7	5.7 (Fc/Fc ⁺)	Pt	[29]
P ₂₂₂₈ NTf ₂	~ -3.2	~3.0	6.2 (Fc/Fc ⁺)	Pt	[29]
P ₂₂₂₍₂₀₁₎ NTf ₂	~ -3.1	~2.2	5.3 (Fc/Fc ⁺)	Pt	[29]
bmim(CF ₃) ₂ PO ₂	~ -2.3	~2.2	4.5 (Ag)	Pt	[21]
bmimOTf	~ -2.2	~2.8	5.0 (Pt)	GC	[25]
emimBF ₄	~ -2.1	~1.9	4.0 (Pt)	GC	[25]
	~0.9	~5.0	4.1 (Li/Li ⁺)	GC	[30]
mpimBF ₄	~1.0	~5.1	4.1 (Li/Li ⁺)	GC	[30]
Bu ₄ NNO ₃	~ -3.0	~1.5	4.5 (SCE)	—	[8]
Bu ₄ PNO ₃	~ -2.0	~1.5	3.5 (SCE)	—	[8]

lanthanides and actinides are less. In addition, the metallic electrodeposition obtained for lanthanides are not usually stable and undergoes oxidation to their respective oxides during electrolysis.

4. Electrochemical Behavior of Lanthanides and Actinides in Ionic Liquids

The electrochemistry of actinides was indeed reported a few decades ago using chloroaluminate-based RTIL as the medium. However, these studies were not directed towards the electrodeposition of actinides, but involved only the

basic understanding of coordination chemistry, solution chemistry, and electrochemical behaviour of metals. In fact, this was due to the inadequacy in the electrochemical window and poor cathodic stability of chloroaluminates. The earliest work on the electrochemistry of uranium in acidic and basic chloroaluminate melt was reported by D'Olieslanger and coworkers [31, 32]. In acidic 2:1 melts (AlCl₃:N-(n-butyl) pyridinium chloride), the reduction of U(IV) to U(III) at glassy carbon electrodes was reported to be irreversible. The formal standard potential of the U(IV)/U(III) redox couple as a function of the melt acidity was determined. U(III) in the melt was found to exist as

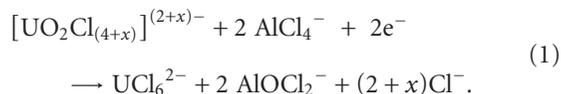
TABLE 3: The abbreviations of the ionic liquids.

Name of the ionic liquid	Abbreviation
1-butyl-3-methylimidazolium chloride	bmimCl
1-butyl-3-methylimidazolium tetrafluoroborate	bmimBF ₄
1-butyl-3-methylimidazolium hexafluorophosphate	bmimPF ₆
1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	bmimNTf ₂
1-butyl-3-methylimidazolium trifluoromethanecarbonate	bmimCF ₃ CO ₂
1-butyl-3-methylimidazolium dicyanamide	bmimDCA
1-hexyl-3-methylimidazolium chloride	hmimCl
1-butyl-2,3-dimethylimidazolium chloride	bdmimBF ₄
Betaine bis(trifluoromethanesulfonyl)imide	HbetNTf ₂
N-butyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide	BMPyNTf ₂
N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide	MPPiNTf ₂
Triethylpentylphosphonium dicyanamide	P ₂₂₂₅ DCA
Triethyldimethyletherphosphonium dicyanamide	P ₂₂₂₍₁₀₁₎ DCA
Triethyldimethyletherammonium dicyanamide	N ₂₂₂₍₁₀₁₎ DCA
Triethylethylmethyletherphosphonium dicyanamide	P ₂₂₂₍₂₀₁₎ DCA
Triethylpentylphosphonium bis(trifluoromethanesulfonyl)imide	P ₂₂₂₅ NTf ₂
Triethyldimethyletherphosphonium bis(trifluoromethanesulfonyl)imide	P ₂₂₂₍₁₀₁₎ NTf ₂
Triethyloctylphosphonium bis(trifluoromethanesulfonyl)imide	P ₂₂₂₈ NTf ₂
Triethylethylmethyletherphosphonium bis(trifluoromethanesulfonyl)imide	P ₂₂₂₍₂₀₁₎ NTf ₂
1-butyl-3-methylimidazolium bis(trifluoromethane)phosphinate	bmim(CF ₃) ₂ PO ₂
1-butyl-3-methylimidazolium bis(trifluoromethane)sulfonate	bmimOTf
1-ethyl-3-methylimidazolium chloride	emimCl
1-ethyl-3-methylimidazolium tetrafluoroborate	emimBF ₄
1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	emimNTf ₂
1-methyl-3-propylimidazolium tetrafluoroborate	mpimBF ₄
Tetrabutylammonium nitrate	Bu ₄ NNO ₃
Tetrabutylphosphonium nitrate	Bu ₄ PNO ₃
Tri-n-butylmethyl ammonium bis(trifluoromethanesulfonyl)imide	Bu ₃ mebu ₃ NNTf ₂
Tri-n-methylbutyl ammonium bis(trifluoromethanesulfonyl)imide	Me ₃ NBuNTf ₂
1-octyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide	OMPpyNTf ₂
N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide	demmaNTf ₂
Tricaprylmethylammonium nitrate	TOMAN
1-butylpyridinium chloride	BuPyCl
1-butylpyridinium tetrafluoroborate	BuPyBF ₄
Tricaprylmethylammonium chloride	Aliquat 336
1-butyl-3-methylimidazolium nonafluorobutanesulfonate	BmimNfO
1-[2-(2-methoxyethoxy)ethyl]-3-methylimidazolium chloride	C ₅ O ₂ ImCl
1-[2-(2-methoxyethoxy)ethyl]-3-methylimidazolium hexafluorophosphate	C ₅ O ₂ ImPF ₆

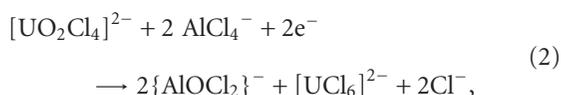
TABLE 4: List of some metals studied for the electrodeposition from room-temperature ionic liquid medium [16, 17].

S. No.	Group	Metals deposited
1	S-block elements	Li, Mg, Cs, and Sr
2	P-block elements	Sn, Al, Al-In, Al-Sb, Al-In-Sb, Al-Si, Ge, Ga, Te, Tl, Pb, Bi, and Si
3	Transition elements	Ti, Ta, Mn, Zn, Zn-Mn alloy, Ru, Rh, Pd, Ag, Au, Co, Co-Zn alloy, Pd-Ag alloy, Pt-Zn alloy, Pt, Pd-In alloy, Ni-Zn alloy, Ni, Zn-Sn alloy, Cd-Te, Cu, Fe, Hg, Cr, and Nb
4	Lanthanides	La, Eu, Nd, and Sm
5	Actinides	U and Th

free U^{3+} ion, and U(IV) as chlorocomplexes, $UCl_x^{(4-x)+}$ with $3 \geq x \geq 1$. The oxidation of U(IV) to U(V) at glassy carbon electrodes was irreversible and dependent on the melt acidity. Further oxidation of U(V) to U(VI) was not feasible due to the anodic instability of the melt. In contrast to acidic melt, U(VI) in basic melt [33] ($AlCl_3 + BuPyCl$), existed as chloro complexes $UO_2Cl_{4+x}^{(2+x)-}$, which underwent a single-step irreversible two-electron transfer to soluble UCl_6^{2-} as shown in (1). The diffusion coefficient was determined to be $2.65 \times 10^{-7} \text{ cm}^2/\text{s}$ in the basic melt (mole ratio of $AlCl_3 : BuPyCl = 0.82 : 1$)



In addition, U(IV) could not be reduced to U(III) in basic melt due to the cathodic instability of $BuPy^+$ cation, which undergoes reduction in preference to U(IV). However, U(VI) could be reduced to U(III) in basic $AlCl_3$ -emimCl [34, 35], as the 1-ethyl-3-methylimidazolium cation ($emim^+$) is more difficult to reduce than the $BuPy^+$ cation. The uranyl ion (UO_2^{2+}) underwent a two electron transfer in basic $AlCl_3$ -emimCl melt followed by the transfer of oxygen to chloroaluminate complex of ionic liquid leading to the formation of $[UCl_6]^{2-}$ as shown in (2) and (3). $[UCl_6]^{2-}$ was then reduced to $[UCl_6]^{3-}$ in the melt



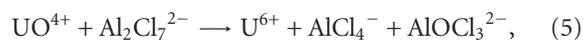
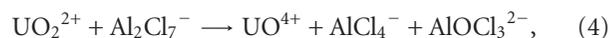
Electrochemical behavior of U(VI) in bmimCl was reported by Giridhar et al. [18]. U(VI) in bmimCl underwent a single-step two-electron transfer reduction to uranium oxide (UO_2) deposit at glassy carbon working electrode. They reported that the electrochemical reduction was not only governed by the diffusion of U(VI), but also by charge transfer kinetics at the working electrode. Thermal analysis of the uranium oxide deposit obtained by the electrolysis of U(VI) from bmimCl revealed the entrapment of nearly 5% bmimCl during electrodeposition.

Ikeda and coworkers [36] developed a new approach for reprocessing spent nuclear fuel using room-temperature ionic liquid as medium. The method involved oxidative dissolution of the spent nuclear fuel by using Cl_2 , followed by the electrochemical reduction of U(VI) to UO_2 . By this method, the electrochemical behavior of UO_2^{2+} in various ionic liquids such as bmimCl, bmimBF₄, and bmimNfO was studied and the two-step reduction of UO_2^{2+} to U(IV) through U(V) was reported. The electrochemical reduction of UO_2^{2+} in bmimNfO at -1.0 V (versus $Ag/AgCl$) produced uranium oxide deposit at carbon electrode. The electrochemical behaviour of $[UO_2Cl_4]^{2-}$ in bmimCl ionic liquid was also reported by Ikeda et al. [37]. The uranium complex, $[UO_2Cl_4]^{2-}$, was dissolved in bmimCl by using $Cs_2UO_2Cl_4$ or $UO_2Cl_2 \cdot nH_2O$ compounds and reported

the quasireversible reduction of $[UO_2Cl_4]^{2-}$ to $[UO_2Cl_4]^{3-}$. Similarly, Ikeda and coauthors [38] studied the dissolution of uranium fluoride (UF_4) in bmimCl by oxidation of U(IV) to U(VI) and the UO_2^{2+} present in bmimCl was reduced to UO_2 by a two-step one electron transfer.

The electrochemical behaviour of neptunium in acidic and basic $AlCl_3$ -1-n-butylpyridinium chloride melt at 313 K was studied by Schoebrechts and Gilbert [39]. In acidic and basic melts, the reduction of Np(IV) to Np(III) at glassy carbon electrode was quasireversible. In basic melt, Np(III) and Np(IV) exist as $NpCl_6^{3-}$ and $NpCl_6^{2-}$, whereas in acidic melt it exist in the form of solvated Np^{3+} and $NpCl_x^{(4-x)-}$ ($3 \geq x \geq 1$). The study showed that the acidic melt acted as a poor solvating medium for neptunium.

Choppin and coworkers [40] have investigated the electrochemistry and spectroscopy of UO_2^{2+} in acidic chloroaluminate medium. UO_2^{2+} in acidic $AlCl_3$ -emimCl melt was gradually reduced to U(V) and it was facilitated only by $AlCl_4^-$ and $Al_2Cl_7^-$ species by the sequence of reactions shown in the following:



Deetlefs et al. studied [41] the electrochemistry of various uranium halide complexes in basic and acidic bromoaluminate (III) imidazolium ionic liquid. U(IV) in the basic ionic liquid was reduced to U(III) and U(VI) to U(IV). Lin and Hussey [42] studied the electrochemical and spectroscopic properties of Ce(III) in basic $AlCl_3$ -emimCl and reported a quasireversible reduction of Ce(IV) to Ce(III) at glassy carbon, Pt and W electrodes.

The redox behavior of actinides in haloaluminate ionic liquids (1st generation) demonstrate that the electrochemical window of haloaluminates permits the redox conversion of An(III) to An(VI) and vice versa, irrespective of the composition of RTIL. Reduction of An(III) to An(0) was not feasible due to inadequate cathodic stability of haloaluminates. A similar behavior could be expected for lanthanides also, as the characteristic trivalents are hard to reduce to metallic state than actinides. The studies reported by Schoebrechts et al. [43, 44] also confirmed that some trivalent lanthanides ions such as Sm(III), Eu(III), Tm(III), and Yb(III) dissolved in acidic $AlCl_3$ -BuPyCl ionic liquid were reduced only to the corresponding divalent ions. Due to these limitations, RTILs did not gain popularity in nonaqueous reprocessing earlier.

Moisture stable ionic liquids were discovered in late 1990s. They are known as 2nd generation ionic liquids. Several RTILs having electrochemical window as large as $\sim 6 \text{ V}$ and extended cathodic stability [45–47] were identified. This factor gave a renaissance to the use of ionic liquids in nonaqueous processing applications. Nikitenko and coworkers [48–50] investigated the spectroscopic and electrochemical aspects of U(IV)-hexachloro complexes in bmimNTf₂, Bu₃MeNNTf₂ hydrophobic ionic liquids. Due to

large electrochemical window of RTIL, it was possible to study the oxidation and reduction behaviour, up to the metallic form. The uranium redox values were reported depend strongly on the type of RTIL cation. $[\text{UCl}_4]^{2-}$ in $\text{Bu}_3\text{MeNNTf}_2$ can be converted to metallic uranium at -3.12 V (versus Fc/Fc^+) at 333 K . Nikitenko and Moisy [50] further investigated the coordination behaviour of $\text{Np}(\text{IV})$ and $\text{Pu}(\text{IV})$ in bmimNTf_2 . The $[\text{NpCl}_6]^{2-}$ and $[\text{PuCl}_6]^{2-}$ complexes are electrochemically inert in bmimNTf_2 at glassy carbon electrode. However, the addition of bmimCl facilitated the quasireversible electrochemical reduction of $\text{Np}(\text{IV})/\text{Np}(\text{III})$ and $\text{Pu}(\text{IV})/\text{Pu}(\text{III})$ and oxidation of $\text{Np}(\text{IV})$ and $\text{Pu}(\text{IV})$. These redox reactions were reported only when $\text{Cl}^-/\text{An}(\text{IV})$ ratio exceeded six in ionic liquid medium.

Bhatt et al. [51–53] studied the electrochemistry of some lanthanide ions, $\text{La}(\text{III})$, $\text{Sm}(\text{III})$, and $\text{Eu}(\text{III})$ in R_4XNTf_2 , where $\text{X} = \text{N}$, P , and As . The RTIL, Me_4XNTf_2 , exhibited a large electrochemical window ($\sim 6\text{ V}$). They also studied [52] the reduction of $\text{La}(\text{III})$, $\text{Sm}(\text{III})$, and $\text{Eu}(\text{III})$ to metallic state in the RTIL, $\text{Me}_3\text{BuNNTf}_2$, and reported similar results as in the previous case. However, it was reported that the deposits were not stable and underwent very fast oxidation to their respective oxides during the course of washing treatment. Moreover, the standard reduction potentials of these lanthanides are nearer or negative to the reduction potential of the ionic liquids. Therefore, the lanthanides electrodeposit obtained using these ionic liquids were not very useful. The voltammetric behavior of $[\text{Th}(\text{NTf}_2)_4(\text{HNTf}_2)] \cdot 2\text{H}_2\text{O}$ was also studied [53] in $\text{Me}_3\text{BuNNTf}_2$. $\text{Th}(\text{IV})$ in this ionic liquid was reduced to $\text{Th}(0)$ by a single-step reduction. The E^0 value for the reduction of $\text{Th}(\text{IV})$ to $\text{Th}(0)$ was determined to be -2.20 V (versus Fc^+/Fc), -1.80 V versus SHE). Due to the presence of moisture in ionic liquid, the reduced product $\text{Th}(0)$ was converted to ThO_2 .

Legeai et al. [54] reported the electrodeposition of lanthanum in OMPyNTf_2 ionic liquid. The authors reported that the wide electrochemical window (4.8 V) and low hygroscopic character of OMPyNTf_2 allowed the electrodeposition of lanthanum without the need of an inert atmosphere. About 350 nm thick lanthanum film on Pt electrode was deposited. Nagaishi et al. [55] studied the physicochemical behaviour, spectroscopic and electrochemical behaviour of $\text{Eu}(\text{III})$ as a function of water in demmaNTf_2 and bmimNTf_2 ionic liquids. The variations in the diffusion coefficient of $\text{Eu}(\text{III})$ in dehydrated and water saturated conditions were reported by the authors. Yamagata et al. [56] studied the electrochemical behaviour of samarium(III), europium(III) and ytterbium(III) in BMPyNTf_2 , and emimNTf_2 ionic liquids. The quasireversible reduction of $\text{Sm}(\text{III})$, $\text{Eu}(\text{III})$ and $\text{Yb}(\text{III})$ to divalent state was reported. The electrochemical behaviour of $\text{Eu}(\text{III})$, $\text{Sm}(\text{III})$, and $\text{Ce}(\text{III})$ in bmimCl ionic liquid at Pt electrode at 373 K was also studied by Jagadeeswara Rao et al. [57]. Again, the reduction of $\text{Eu}(\text{III})$, $\text{Sm}(\text{III})$, and $\text{Ce}(\text{III})$ to the corresponding divalent ions was quasireversible. The apparent standard potentials and the thermodynamic parameters for the reduction reaction were determined and reported in this paper. Matsumiya et al. [58] reported the electrochemical

behavior of $\text{Eu}(\text{III})$ and $\text{Sm}(\text{III})$ in ionic liquids, $\text{P}_{2225}\text{NTf}_2$ and $\text{N}_{2225}\text{NTf}_2$. From the redox potentials, the authors reported that the donor property of phosphonium-based ionic liquids was slightly larger than that of nitrogen-based ionic liquids.

The electrochemical behavior of $\text{Eu}(\text{III})$ [24] and $\text{U}(\text{IV})$ [59] in BMPyNTf_2 and MPPiNTf_2 , respectively, was studied by Jagadeeswara Rao et al. The europium oxide (Eu_2O_3) and uranium oxide (UO_2) were dissolved in RTIL medium and the electrochemical behavior of $\text{Eu}(\text{III})$ in BMPyNTf_2 and $\text{U}(\text{IV})$ in MPPiNTf_2 was studied by various transient electrochemical techniques. The metallic nature of europium and uranium deposit obtained in the study was confirmed by XRD and EDXRF techniques. The study established the feasibility of dissolving the lanthanide and actinide oxides in ionic liquid medium and recovery in metallic form by electrodeposition. Joseph et al. [60] studied the lithium-assisted electrochemical reduction of U_3O_8 in MPPiNTf_2 to explore the feasibility of using RTILs for direct electrochemical reduction of uranium oxide at near ambient temperature. The electrochemical behavior of Li^+ in MPPiNTf_2 at stainless steel electrode was investigated by cyclic voltammetry and chronoamperometry. Electrodeposition of metallic lithium on U_3O_8 particles contained in a stainless steel basket was carried out to examine the feasibility of reducing U_3O_8 to metallic form. The results indicated the feasibility of reducing bulk of U_3O_8 to UO_2 at near ambient temperature. However, reduction of UO_2 to metallic form was not observed under the present conditions.

5. Electrochemical Behavior of Fission Products in Ionic Liquids

5.1. Cesium and Strontium. Cesium-137 and Strontium-90 are the major radiotoxic fission product isotopes present in high-level liquid waste. Chen and Hussey [61] studied the electrochemistry of the electropositive fission product, Cs , at mercury electrode using $\text{Bu}_3\text{MeNNTf}_2$ by various voltammetric techniques. The reduction of Cs^+ at mercury electrode was quasireversible and a diffusion coefficient of $\sim 10^{-8}\text{ cm}^2/\text{s}$ at 303 K was reported. Deposition/stripping was conducted at mercury film electrode with recovery of 97% of loaded cesium.

Chen and Hussey [62] also reported the selective extraction of Cs^+ and Sr^{2+} from aqueous solutions by using the ionophores calix[4]arene-bis(*tert*-octylbenzo-crown-6) (BOBCalixC6) and dicyclohexano-18-crown-6 (DCH18C6), respectively, present in the hydrophobic, ionic liquid, $\text{Bu}_3\text{MeNNTf}_2$. The electrochemistry of Cs^+ coordinated by BOBCalixC6 and Sr^{2+} coordinated by DCH18C6 was examined at mercury film electrode (MFE) by using cyclic staircase voltammetry, sampled current voltammetry at a rotating electrode, and chronoamperometry. Both $\text{BOBCalixC6} \cdot 2\text{Cs}^+$ and $\text{DCH18C6} \cdot \text{Sr}^{2+}$ exhibited well-defined reduction waves at approximately -2.4 and -2.9 V versus the ferrocene/ferrocenium (Fc/Fc^+) couple, respectively. The coordinated metals were reduced to their respective amalgams, permitting the recycling of the ionophores.

Chen [63] reported the extraction of Sr^{2+} and Cs^+ from aqueous solutions by using the ionophores dicyclohexano-18-crown-6 (DCH18C6) and calix[4]arene-bis(tert-octylbenzo-crown-6) (BOBCalixC6), respectively, in the hydrophobic, ionic liquid, $\text{Bu}_3\text{MeNNTf}_2$. The possibility of using the electrodeposition technique to recycle the ionic liquid and the ionophores employed for extraction of Sr^{2+} and Cs^+ ions was explored.

5.2. Platinum Group Metals. Spent nuclear fuel is composed of strategic metals such as uranium, and plutonium and potentially useful fission byproducts such as palladium, ruthenium, and rhodium. Significant quantities of platinum groups metals (PGMs) are produced as fission products [64]. Most of the fission PGM isotopes in the spent nuclear fuel are nonradioactive or very weakly radioactive. These fission PGM's are routed to high-level liquid waste (HLLW) during reprocessing of the spent nuclear fuel. Therefore, the HLLW as well as the spent nuclear fuel itself are the valuable resources of man-made noble metals.

Recovery of valuable PGMs from nuclear HLLW was extensively studied [65–70] in the last two decades with particular interest in the separation of palladium. Several authors have reported the electrochemical recovery of PGMs from nitric acid medium [71–75]. Kirshin and Pokhitonov [73] studied the electrolytic recovery of palladium from nitric acid solutions and reported the efficiency of the process in the presence of HNO_3 , NaNO_3 , uranium, and other admixtures. Varentsov and Varentsova [74] reported the electrodeposition of rhodium on carbon fiber electrodes from nitric acid and confirmed that speciation of rhodium strongly affects the deposition behavior. Koizumi and Kawata [75] reported the electrolytic extraction of fission platinoids from nitric acid medium. Recoveries of 90%, 23%, and 10% were reported, respectively, for the deposition of Pd, Rh, and Ru, and the deposition rates were reported to decrease with increase in nitric acid concentration.

The electrochemical behavior of PGMs, namely, ruthenium (III), rhodium (III), and palladium (II) in HLLW as well as ionic liquid medium was studied by Jayakumar et al. [76, 77]. Palladium (II) present in nitric acid medium underwent an irreversible single-step two-electron transfer to metallic palladium at stainless steel electrode, and it was quantitatively recovered by electrolysis at -0.5 V (versus Pd). However, several complications aggravated in the presence of interfering metal ions such as silver, nitrate, and iron that are likely to present in HLLW during electrolysis. As a result, the recovery and Faradaic efficiency was dropped below 30% when electrolysis was carried out with simulated wastes.

Later a novel approach, extraction-electrodeposition (EX-EL) method, was developed by the same group for the quantitative recovery of palladium from simulated HLLW using room-temperature ionic liquid as medium [78]. Initially, Giridhar et al. [79] reported the extraction-electrodeposition (EX-EL) for the separation and recovery of palladium from nitric acid medium using TOMAN ionic liquid. Later, Jayakumar et al. [78] studied the EX-EL process for the recovery of palladium from high-level liquid waste in

detail. The process exploited a few remarkable properties of room-temperature ionic liquid, namely, liquid ion exchange behavior and wide electrochemical window to develop a simplified procedure for quantitative recovery of palladium. More than 60% of palladium was extracted using 0.5 M TOMAN/ CHCl_3 in a single contact and complete extraction was achieved in five contacts. The extracted palladium was quantitatively recovered by electrodeposition at stainless steel electrode.

The electrochemical behaviour of Pd(II), Ru(III) and Rh(III) in ionic liquid is required to understand the feasibility of recovering these noble metals directly from the spent nuclear fuel by nonaqueous processing routes. In this context, the electrochemical behavior of palladium(II) in the basic aluminium chloride + emimCl ionic liquid at glassy carbon, tungsten, and platinum electrodes was reported by Sun and Hussey [80]. A single-step two-electron reduction of Pd(II) to Pd(0) was reported. In addition, a nucleation loop was also observed. Hussey et al. [81] reported an electrochemical study of the ruthenium(III) and (IV) hexachlorometallates in a basic room-temperature chloroaluminate molten salt. Ruthenium(IV) showed a couple of reduction waves in the cyclic voltammogram. The first wave corresponds to the reduction of Ru(IV) to Ru(III) and the second reduction was attributed to the multielectron reduction of Ru(III) to other unknown ruthenium complexes. De long et al. [82, 83] studied the electrodeposition of palladium from AlCl_3 -emimCl ionic liquid and adsorption of palladium chloride on solid electrodes. Electrodeposition of palladium in the melt was dependent on the mole fraction of AlCl_3 and the reduction potential was shifted to $\sim +2.0\text{ V}$, when the melt was changed from basic to acidic.

Crisp et al. [84] reported the reduction of dioxotetrachlororuthenate(VI) to hexachlororuthenate(IV) in a basic 1-butylpyridinium chloride-aluminum(III) chloride ionic liquid. The authors have indicated that the redox system was the first irreversible transfer of an oxide ion from a tetrachloroaluminate in an ambient temperature ionic liquid. Electrodeposition of palladium-silver [85] and palladium-indium [86] from a Lewis basic emimCl/emimBF₄ ionic liquid was reported by Sun and coworkers. Since the reduction potentials of Ag(I) and Pd(II) were very close to each other and alloy formation was observed [87]. In the case of palladium-indium [86], over potential deposition (OPD) of palladium was reported in the presence of indium; however, underpotential deposition was observed for indium in the presence of palladium.

Bando et al. [88] investigated the electrodeposition of palladium in a hydrophobic BMPyNTf₂ room-temperature ionic liquid. The irreversible reduction of PdBr_4^{2-} and PdCl_4^{2-} to Pd(0) was observed in this ionic liquid, and the authors have reported that the reduction potential of PdCl_4^{2-} was more negative than that of PdBr_4^{2-} , reflecting the difference in the donor property between chloride and bromide. Giridhar et al. studied the feasibility of recovering fission palladium from bmimCl medium [85] and extraction-electrodeposition procedure using Aliquat 336 ionic liquid [79]. However, the electrochemical behavior of Pd(II), Rh(III), and Ru(III) in bmimCl was studied in detail

by Jayakumar et al. [89–91]. Electrowinning of palladium was conveniently carried out at -0.8 V (versus Pd) at stainless steel electrode, whereas the electrodeposition of rhodium was feasible only at -1.6 V . In contrast to both these metal ions, ruthenium (III) formed a stable solution with bmimCl, and reduction of Ru (III) in to metallic form was not feasible in bmimCl. However, coexistence of palladium (II) in bmimCl favored underpotential deposition of ruthenium and rhodium. Initial deposition of palladium on working electrode seems to shift the deposition potentials of ruthenium (III) and rhodium (III) and favored underpotential deposition by more than 1 V . The study established the feasibility of using bmimCl ionic liquid as electrolyte for the electrochemical recovery of fission platinoids at 373 K .

Raz et al. [92] studied the electrodeposition of ruthenium on n-type silicon from bmimPF₆. The reduction of ruthenium occurred at -2.1 V (versus Pt) and the stripping at 0.2 V (versus Pt). Metallic Ru film of $\sim 100\text{ nm}$ thickness was deposited and characterized by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). Mann et al. [93] studied the electrodeposition of ultra thin ruthenium films on Au(111) substrate from bmimDCA ionic liquid medium. Matsumiya et al. [58] reported the electrochemical behavior of $[\text{PdCl}_4]^{2-}$ and $[\text{PdBr}_4]^{2-}$ in room-temperature ionic liquids, P₂₂₂₅NTf₂, P₂₂₂₍₁₂₎NTf₂, and N₂₂₂₅NTf₂. They mentioned that the diffusion coefficients of palladium complex in phosphonium-based ionic liquids were slightly larger than those in corresponding ammonium counterparts and close to those in BMPyNTf₂.

5.3. Thermal and Radiation Stability. Ionic liquids with good radiation and thermal stability are indeed necessary for nuclear fuel cycle applications. Moura Ramos et al. [94] investigated the glass transition of imidazolium-based RTILs such as C₅O₂ImCl and C₅O₂ImPF₆⁻ and reported the heat capacity jump during glass transition. Zhang et al. [95, 96] determined the molar heat capacities of BuPyBF₄ and bmimBF₄ using adiabatic calorimeter and reported the enthalpy and entropy change during glass transition of RTIL. Reddy and coworkers [97] reported some thermodynamic properties of bmimCl determined by using techniques such as TG, DTA, and DSC. Jagadeeswara Rao et al. [98] reported the thermal stabilities and heat capacities of various ionic liquids such as MPPiNTf₂, BMPyNTf₂, and HbetNTf₂. The ionic liquids, MPPiNTf₂, and BMPyNTf₂, were reported to be thermally stable up to 650 K , whereas HbetNTf₂ was stable only up to 560 K .

Allen et al. [99] investigated the radiation stability of 1, 3-dialkylimidazolium nitrate/chloride ionic liquids and reported that their stabilities are comparable with that of benzene and more stable than the mixtures of tributylphosphate and odourless kerosene under similar irradiation conditions. These ionic liquids were reported as radiation resistant up to 400 kGy , and it was attributed to the combination of properties of a salt and aromaticity. Berthon et al. [100] studied the gamma radiolysis of hydrophobic ionic liquids bmimPF₆ and bmimNTf₂. It was reported that the properties such as density, surface tension, and refractive

index were unchanged upon irradiation; however, significant increase in viscosities and lowering of conductivity was observed in case of irradiated RTILs. Moreover, the overall concentrations of radiolysis products did not exceed $1\text{ mol}\%$ when irradiated up to 1200 kGy . Jagadeeswara Rao et al. [22] also reported a similar observation for the ionic liquids such as, bmimCl, hmimCl, HbetNTf₂, BMPyNTf₂, MPPiNTf₂, and aliquat 336 ionic liquids upon gamma irradiation.

Lall-Ramnarine et al. [101] investigated pulse radiolysis of bis(oxalato)borate anion-based ionic liquids. Efficient scavenging of radiolytically generated electrons was observed in these ionic liquids. It was suggested that these borated ionic liquids may find useful applications during handling of concentrated fissile elements. Tarábek et al. [102] studied the electron beam radiolysis of several NTf₂⁻-based ionic liquids. The study revealed that the formation of hydrogen gas due to radiolysis of ionic liquids was relatively low compared to aliphatic and aromatic organic compounds. Ionic liquids with imidazolium and pyridinium cations were reported to give smallest hydrogen yields. Yuan et al. [103] studied the gamma radiolysis of bmimNTf₂. It was reported that the absorbance of ionic liquids at 290 nm increased with increase of absorbed dose, and it was attributed to the radiolysis of bmim⁺ cation. Qi et al. [104] studied the gamma radiation effect on bmimBF₄. They reported that the irradiation-induced darkness and increased the UV absorption, but it did not affect the glass transition point of bmimBF₄. They concluded that the radiation stability of bmimBF₄ was higher than bmimPF₆.

6. Conclusions

RTILs initially introduced as a substitute to the molecular diluent, n-dodecane, in aqueous reprocessing applications, are now receiving an upsurge in the studies related to nonaqueous reprocessing. The discovery of the moisture stable ionic liquids in late 1990s having wide electrochemical window ($\sim 6\text{ V}$) and excellent cathodic stability indeed boosted the ionic liquid research for such applications. The electrochemical behavior of actinides and fission products in moisture stable ionic liquids reported so far are encouraging, and, going by the research work published recently, it appears that ionic liquids have good potential for nonaqueous processing applications. While these new results and novel technologies exhibit a great potential, the physical and chemical properties of the ionic liquid needs to be tuned to suit the ionic liquid for robust applications. It is, therefore, recommended to study the fundamental properties of ionic liquids that govern electrochemical stability, solubility of actinides and fission products, viscosity, and so forth to design RTILs having all the required properties for the desirable applications.

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