

SUPPLEMENTAL INFORMATION

Tandem Dissolution Of UO_3 in Amide-Based Acidic Ionic Liquid and in-situ Electrodeposition Of UO_2 with Regeneration of the Ionic Liquid: A Closed Cycle

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KEYWORDS: Acidic ionic liquids, Uranium Dioxide, Dissolution, electrodeposition

Supporting Information Placeholder

1 EXPERIMENTAL

2 General Methods and Materials

3 All the chemicals and reagents used in this
4 study were of analytical grade unless otherwise
5 specified. Depleted uranium trioxide (UO_3) and
6 uranium dioxide (UO_2) were obtained from the Fuel
7 Cycle and Isotopes Division, Oak Ridge National
8 Laboratory. Ethyl imidazole (99%), bromoethane
9 (99%), and anhydrous tetrahydrofuran (THF) (99.9%)
10 were purchased from Sigma Aldrich, St. Louis, MO,
11 USA. Lithium bis(trifluoromethanesulfonyl)imide
12 (LiNTf_2) (99%) was obtained from 3M Performance
13 Chemical Products Division, St Paul MN.
14 Bis(trifluoromethanesulfonyl)imide (HNTf_2) (99%)
15 80% aqueous solution was obtained from Ionic
16 Liquids Technologies, Tuscaloosa, AL, USA.

17 Synthesis of 1-ethyl-3-methylimidazolium

18 bis(trifluoromethanesulfonyl)imide ($[\text{EMIM}][\text{NTf}_2]$).

19 The ionic liquid $[\text{EMIM}][\text{NTf}_2]$ was
20 synthesized according to a modified procedure
21 reported in the literature [1]. In a 300 mL round-
22 bottom flask, methyl imidazole (20.0 g, 243.0 mmol)
23 was allowed to react with 1-bromoethane (34.0 g,
24 312.0 mmol) in dry THF (50 mL) under a stream of
25 nitrogen gas. The mixture was allowed to stir
26 vigorously at room temperature for 24 h, and the
27 resulting white precipitate was isolated and washed
28 repeatedly with ethyl acetate (3 × 100 mL) to remove
29 any unreacted starting materials. Then the
30 $[\text{EMIM}][\text{Br}]$ salt was dried under vacuum (yield 90%).
31 A portion of the resulting $[\text{EMIM}][\text{Br}]$ salt (20.0 g,

32 105.0 mmol) was mixed with LiNTf_2 (45.0 g, 156.8
33 mmol) in 20 mL of water and stirred overnight to
34 obtain $[\text{EMIM}][\text{NTf}_2]$ as a colorless liquid. ¹H-NMR
35 (400 MHz, DMSO-d_6): δ 9.10 (s, 1H), 7.75 (s, 1H), 7.67
36 (s, 1H), 4.19 (q, $J = 7.2$ Hz, 2H), 3.85 (s, 3H), 1.42 (t, J
37 = 7.2 Hz, 3H). The ionic liquid was dried in vacuo at
38 333 K for 24 h. The water content of this ionic liquid
39 was determined by Karl Fisher titration method and
40 found to be 20 ppm.

41 Synthesis of N,N-dimethylacetamidium

42 bis(trifluoromethylsulfonyl)imide ($[\text{DMAH}][\text{NTf}_2]$)

43 The synthesis of this protic ionic liquid is
44 based on previous literature. [1] The conjugate bases
45 of the organic amides were mixed with concentrated
46 HCl at ambient temperature. To this, a solution of
47 LiNTf_2 was added in equal molar ratios. A denser IL
48 phase formed at the bottom of the flask and was
49 separated from the top aqueous phase and then
50 washed with D.I. water to remove LiCl. The product
51 was then dried under vacuum at 70 C for 4 h.

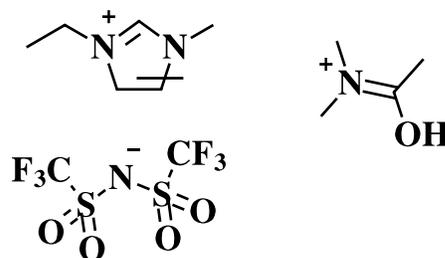


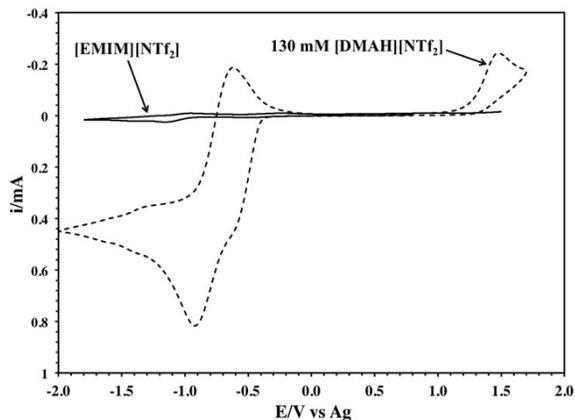
Figure S1. Structures of ionic liquid constituents.

55 Synthesis and characterization of uranyl 108
56 bis(trifluoromethanesulfonyl)imide [UO₂(NTf₂)₂]. 109
57 Uranyl bis(trifluoromethanesulfonyl)imide 110
58 was synthesized according to a slightly modified 111
59 procedure reported in the literature. [2]UO₃ (1.0 g) 112
60 was allowed to dissolve in an 80% solution of 113
61 bis(trifluoromethanesulfonyl)imide (10 mL) by 114
62 vigorous stirring at 50 °C for 3 d. The temperature 115
63 was then raised to 80 °C, and the mixture was 116
64 refluxed for overnight, after which the water and 117
65 unreacted HNTf₂ acid were removed by distillation 118
66 under vacuum. The acidic impurities (HNTf₂) present 119
67 in the system were extracted with dichloromethane 120
68 (3 × 20 mL), and the resulting thick, viscous crude 121
69 material was redissolved in ethanol and filtered 122
70 through a fine crucible to remove any unreacted 123
71 UO₃. The resulting dark-yellow viscous liquid was 124
72 dried under vacuum over P₂O₅ at 100 °C for 60 h prior 125
73 to use. Standardization of the UO₂(NTf₂)₂ was 126
74 accomplished spectrophotometrically by dissolving 127
75 the glassy material in 1 M HCl in the presence of 128
76 arsenazo-III and taking absorbance measurements 129
77 using the USB4000-VIS-NIR spectrophotometer in a 130
78 1 cm quartz cell. This is a modification of a previous 131
79 procedure [3] where 3 M HClO₄ was used as the 132
80 matrix. The uranyl salt contained 6% excess mass 133
81 which we attribute to water, leading us to formulate 134
82 the isolated material as UO₂(NTf₂)₂•2H₂O. 135
83 Electrochemical experiments 136
84 Electrochemical experiments were 137
85 performed using a 600 D potentiostat purchased 138
86 from CH Instruments, Inc. Austin, TX, USA. Cyclic 139
87 voltammetry experiments were performed in a 140
88 single-cell compartment cell using a platinum disk (d 141
89 = 2mm, CH Instruments) working electrode (WE), 142
90 platinum wire counter electrode (CE), and Ag wire 143
91 quasi-reference electrode (RE). The Pt disk electrode 144
92 was polished prior to every set of CV experiments, on 145
93 emory papers, with varying granular sizes followed 146
94 by polishing on a slurry of 5 μm alumina powder. In 147
95 addition to mechanical polishing, the electrode 148
96 surface was pretreated in 5 M H₂SO₄ by applying a
97 cathodic potential of -1.0 V vs. Ag for 1 h to further
98 ensure a Pt metal electrode surface.[4-6] This 1 h
99 pretreatment was necessary to achieve more
100 reproducible results. The pretreated electrode was
101 dipped in neat [EMIM][NTf₂] before measurements
102 were taken. Repeated argon-purge and vacuum
103 cycles were performed over a period of 15-30 min. to
104 effectively drive off dissolved oxygen and residual
105 water from the RTIL system in the electrochemical
106 cell. In addition, the [EMIM][NTf₂] is stored in an
107 amber vial and heated to 110 °C for 30-60 minutes

prior to each experiment. The electrochemical cell
(15 mL volume) used for the controlled-potential
experiment was composed of three compartments
separated by 5 μm pore glass frits. All the
electrochemical measurements were performed
under an argon (99.999%) atmosphere.

Cyclic voltammetry (CV)

Vacuum-dried UO₂(NTf₂)₂ was dissolved in
[EMIM][NTf₂] to yield 50 mM solutions. CV
experiments were performed at 100 °C using a
thermostated hot plate with a glass cell and
scanning rate of 100 mV s⁻¹. The cathodic and
anodic limits were determined by performing CV
analysis on neat [EMIM][NTf₂] ionic liquid. The
cathodic limit was considered to be the potential at
which reduction of the imidazolium cation
commences (ca. -1.6 V, -40 μA), and the anodic limit
(+1.8 V, 40 μA) was considered to be the potential at
which the oxidization of the NTf₂⁻ anion
commences. To reference the Ag pseudo reference
electrode in the ionic liquid, the
ferrocene/ferrocenium (Fc⁺/Fc) couple was used as an
internal standard. The Fc⁺ reduction at 100 °C was
observed at +0.04 V at the Pt working electrode,
while the Fc oxidation was observed at +0.14 V,
resulting in a peak-to-peak separation of 100 mV for
the Fc⁺/Fc redox couple (E_{1/2} = +0.09 V vs Ag), which
is slightly greater than the theoretical value of 73.9
mV. Furthermore, the redox peaks of (Fc⁺/Fc) couple
do not shift under continual cycling at 100 mV s⁻¹ for
20 cycles, indicating that the Ag pseudo reference
electrode is stable and scan-rate independent for the
electrochemical studies in this work. Over the course
of a two month period, the stability of the Ag wire
was tested using the Fc⁺/Fc couple. The fluctuations
of the formal potential were ±10 mV. The potential
stability of the Ag pseudo reference electrode was
also seen in the consistency of peak positions in the
CV of U(VI) solutions from experiment to
experiment. All potentials given henceforth are
relative to the Ag wire pseudo reference.



149
150 Figure S2. Cyclic voltammograms of 130 mM
151 [DMAH][NTf₂] in [EMIM][NTf₂] at a scan rate of 100
152 mV s⁻¹ and 100°C. Anodic wave of [DMAH][NTf₂]
153 shown as comparison against second anodic wave in
154 Figure 3B.

155 Controlled-potential electrolysis (CPE)

156 The 80 mM UO₂(NTf₂)₂ in solution obtained
157 by dissolving 0.125 g of UO₃ (s) in 5.0 mL of
158 [EMIM][NTf₂] containing 0.257 g of [DMAH][NTf₂]
159 After 24 h, water was driven off by drying the
160 contents under vacuum overnight. Then this solution
161 was loaded into a three-compartment cell in which
162 the cells are separated by glass frits. The CE and RE
163 compartments were filled with dry [EMIM][NTf₂] (ca.
164 5 mL). The electrolysis experiments were carried out
165 with a Pt plate as the WE and platinum gauze as CE.
166 The potential was held at -1.00 ± 0.01 V versus Ag RE
167 at 115 °C for 24 h. A higher temperature was used in
168 the CPE to enhance the mass transfer, accelerating
169 the electrolysis process. The Pt sheet and gauze
170 electrodes used for CPE were pretreated with 0.1 M
171 HNO₃ and then 1.0 M HNO₃, rinsed with deionized
172 water, and dried using a hot stream of air prior to
173 use. After completion of the CPE, the working
174 electrode was rinsed thoroughly with acetone and
175 dried under vacuum prior to recording the weight
176 gain. The solids suspended in solution or at the
177 bottom of the cell were collected by filtration,
178 washed into a vial with acetone, centrifuged, and
179 dried under vacuum prior to recording the mass.

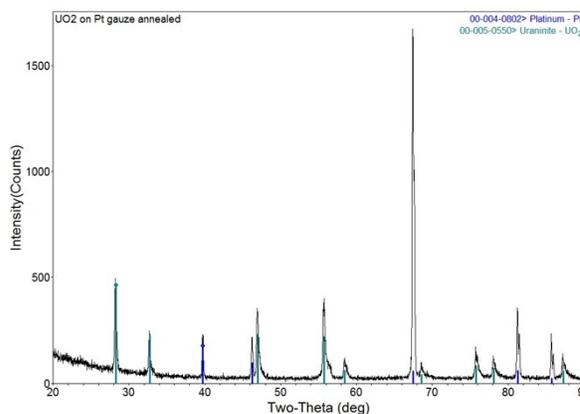
180 XRD analysis

181 Continuous θ-2θ scans were performed on the
182 PANalytical Xpert diffractometer equipped with an
183 X'Celerator detector from nominally 20° to 90° 2θ in
184 30 min. scans using CuKα radiation (λ = 1.540598 Å)
185 and the X'Celerator detector. All scans used ½° fixed
186 slits and 1° anti-scatter slit. A search match was
187 conducted using the "Jade" and/or HighScore
188 software and the International Center for Diffraction
189 Data (ICDD) database. "HighScore Plus" software

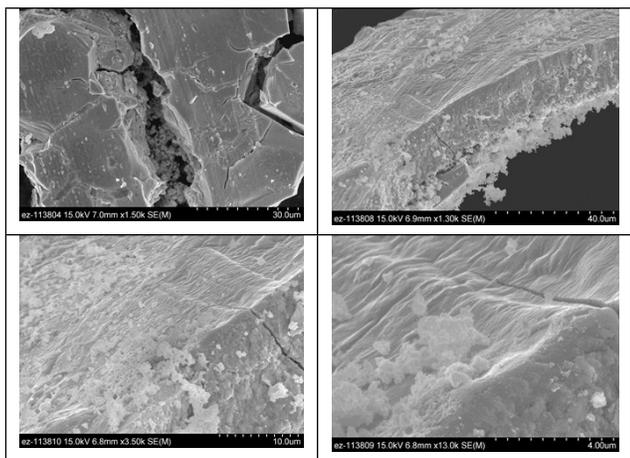
190 was used for crystallographic analysis. The Pt
191 electrode containing the uranium deposit was placed
192 in the sample compartment of the XRD instrument,
193 and the diffraction pattern was obtained at 298 K. A
194 Pt electrode without any deposit was also subjected
195 to XRD for comparison.

196 General Characterization Experiments

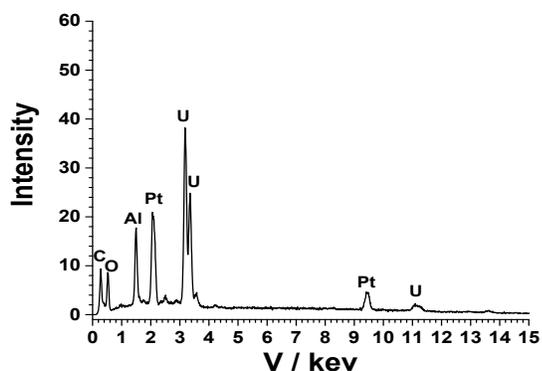
197 ¹H NMR experiments were carried out on a
198 Bruker Avance 400 MHz spectrometer. The water
199 content of the IL was determined by the Karl Fischer
200 method using a CSC Aquapal coulometric titrator.
201 The absorption spectra were recorded using a
202 USB4000-VIS-NIR spectrophotometer (Ocean
203 Optics, Dunedin, FL, USA) equipped with a
204 tungsten-halogen source and fiber optics. The
205 optical path length of the UV transparent quartz
206 cells was 1.0 cm. Annealing of the uranium oxide
207 samples was performed in a tube furnace (Thermo
208 Fisher-Lindburg/Blue) at 1173 K by heat treatment (5
209 K min⁻¹ to 1173 K and hold for 4 h at 1173 K followed
210 by cooling to room temperature). A Hitachi S-3800
211 scanning electron microscopy (SEM) coupled with an
212 energy-dispersive spectrometer (EDS) was used to
213 examine the morphology of the uranium deposit
214 obtained. The voltage of the SEM was set at 10 kV
215 during recording images.



216
217 Figure S3. Powder XRD analysis of the UO₂ deposit
218 obtained after the bulk electrolysis. Due to the
219 irregular surface of the Pt gauze substrate, the XRD
220 data was collected using the mirror optics to
221 minimize the effects of sample surface displacement
222 on peak position. The platinum substrate displayed
223 some preferred orientation in the (022) direction
224 during refinement and the surface material refined
225 as cubic uranite, UO₂, with a = 3.923 Å.



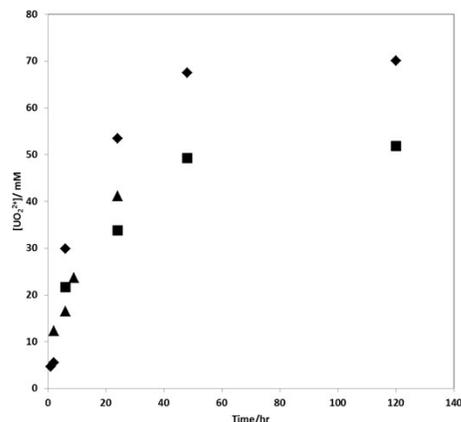
226
227 Figure S4. SEM micrographs of uranium deposits
228 obtained after bulk electrolysis. [7]



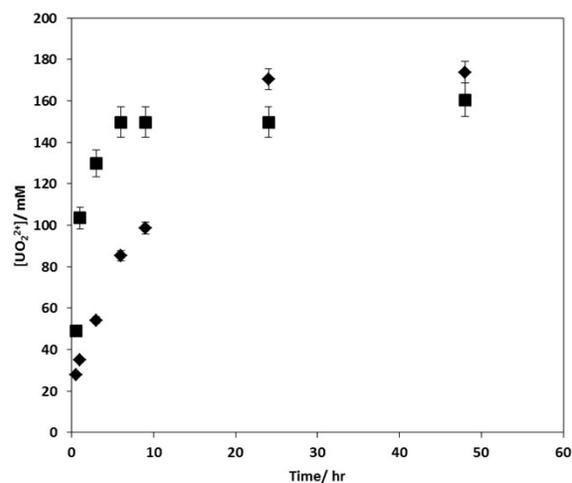
229
230 Figure S5. Energy-dispersive X-ray spectroscopy
231 (EDS) analysis of UO_2 deposit on Pt foil.

232 Dissolution

233 The dissolution of UO_3 was performed at 115
234 °C with three different acidic IL systems (HNTf_2 ,
235 $[\text{DMAH}][\text{NTf}_2]$, and HNTf_2 with DMA) in a sealed
236 system (Figure S6) and also with the acidic ionic
237 liquid $[\text{DMAH}][\text{NTf}_2]$ in $[\text{EMIM}][\text{NTf}_2]$ with and
238 without the use of an argon purge gas (Figure S7).
239 The solution bound species, UO_2^{2+} was monitored via
240 spectrophotometric measurement using a USB4000
241 VIS-NIR spectrophotometer (Ocean Optics, Dunedin,
242 FL, USA) equipped with a tungsten-halogen source
243 and fiber optics.



244
245 Figure S6. Dissolution UO_3 at 115 °C in $[\text{EMIM}][\text{NTf}_2]$
246 with different AIL systems (⊕) HNTf_2 +DMA,
247 (⊙) $[\text{DMAH}][\text{NTf}_2]$, and (⊖) HNTf_2 . Initial $[\text{H}^+] = 150$
248 mM and 100 mg UO_3 . Special note, these systems
249 are closed.
250



251
252 Figure S7. Dissolution of UO_3 as a function of time in
253 $[\text{EMIM}][\text{NTf}_2]$ at 115 °C with (⊕) and without (⊖) an
254 argon purge gas. Concentration of UO_2^{2+} represented
255 as millimolar (mM). Initial concentration $[\text{DMAH}] =$
256 347 mM with 200 mg UO_3 .

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Table S1. Dissolution of UO_3 by acidic ionic liquid [HDMA][NTf₂]

Sample	1	2	3	4	5	6	
UO_3 (mg)		25	50	75	100	125	150
UO_3 (mmol)		0.087	0.174	0.262	0.350	0.437	0.524
[HDMA][NTf ₂] (mg)		257.7	257.7	257.7	257.7	257.7	257.7
[HDMA][NTf ₂] (mmol)		0.699	0.699	0.699	0.699	0.699	0.699
[EMIM][NTf ₂] (g)		5	5	5	5	5	5