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Title: Development of Ionic Liquids for the Electrochemical Separations of Actinides

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Development of Ionic Liquids for the Electrochemical Separations of Actinides

George S. Goff, Xiao-Yan Chen, Kristy M. Long, William C. Ewing, Gordon D. Jarvinen, and Wolfgang Runde

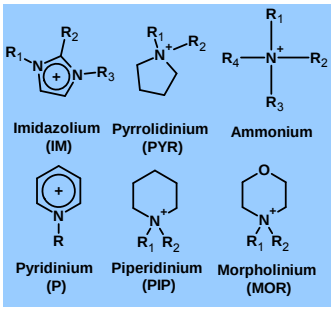
Los Alamos National Laboratory

36th Actinide Separations Conference

Outline

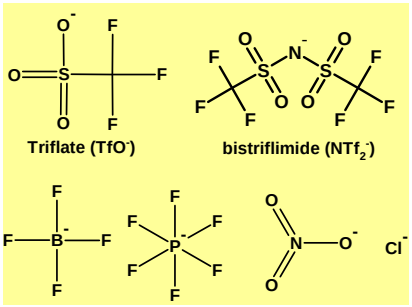
- Background
- IL Applications in Nuclear Fuel Cycles
- Electrochemical Windows of ILs
- Uranium electrochemistry
- Electroplating of UO_2
- Conclusions

What are Ionic Liquids (ILs)?



Common IL cations

Ionic liquids are low-melting salts commonly consisting of an (asymmetrical) organic cation and an inorganic anion.



Common IL anions

Benefits of Ionic Liquids

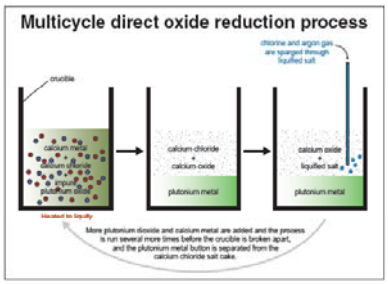
1) Negligible vapor pressure
2) Non-flammable and non-corrosive
3) Large thermal stability (ca. 300 ˚C) and electrochemical windows (up to 6 V)
4) Higher criticality limits than organics
5) Tunable physical and chemical properties (viscosity, electrochemical windows)
6) Organic and inorganic ions

Potential Separations Techniques

1) Solvent Extraction
2) Ion Exchange
3) Dissolution
4) Crystallization Solvent
5) Electrochemistry

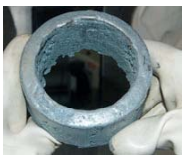
ILs as Alternatives for Nuclear Materials Processing

Direct Oxide Reduction (DOR):

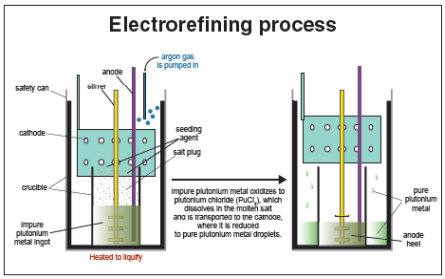


*Actinide Research Quarterly, **3**, 2008*

Pu processing at TA-55
T ≥800°C



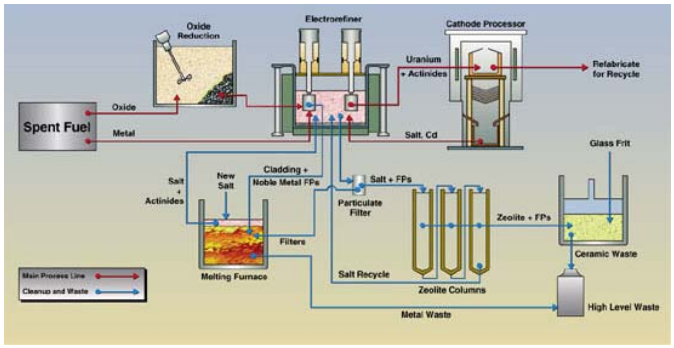
Electrorefining (ER):



*Actinide Research Quarterly, **3**, 2008*

Pyroprocessing of Spent Nuclear Fuel:

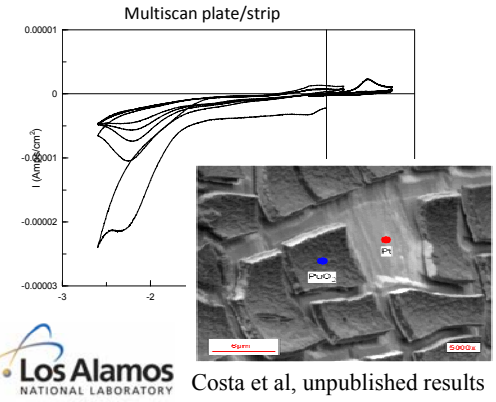
Dissolution ≥500°C



ANL, http://www.anl.gov/Media_Center/Frontiers/2002/d1ee4.html

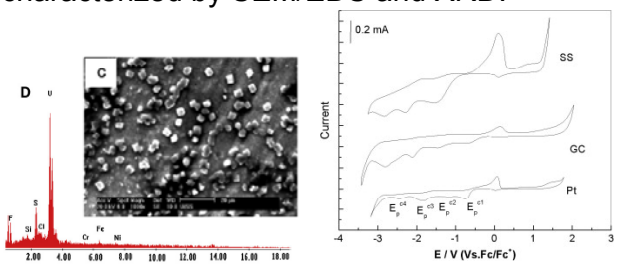
An-IL Electrochemistry

- ILs have been used to electroplate electropositive metals like Li and Na. (Howlett et al 2004, Wibowo et al 2010)
- Very few reports of electroplating lanthanide metals (Bhatt et al 2005, Legei et al 2008), thorium metal (Bhatt et al 2006), and uranium oxide (Giridhar et al 2007, Zhang 2011).
- Costa et al (LANL) showed Pu deposition from DMSO using an IL as the electrolyte. Studies were unsuccessful in ILs due to U and Pu reacting with the anions to form a passivated fluoride layer.



Costa et al, unpublished results

- First report of U metal deposition from an the IL propyl-methyl-piperadinium Tf_2N (Rao et al 2011). Deposition performed at 100°C and characterized by SEM/EDS and XRD.



Electrochemical Windows of Ionic Liquids

- ECW = $E_{pa} - E_{pc}$ (for our work defined as ~0.5 mA/cm^2 with 25 mV/sec scan rate)
  - Typically use a quasi-reference electrode (e.g. Ag wire) sometimes with Fc/Fc^+
  - Most commonly used electrodes include Pt, Glassy Carbon, Au, W
  - Little to no work done on temperature dependence

General trends for electrochemical windows:

Pyridinium < Imidazolium ≤ Sulfonium ≤ Pyrrolidinium ≤ Ammonium/Piperidinium < Phosphonium

Anion stability towards oxidation:

Halide < Chloroaluminate ≤ Fluorinated Anions (PF_6^-) ≤ Triflate/Bistriflimide/Fluoroborates(BF_4^-)

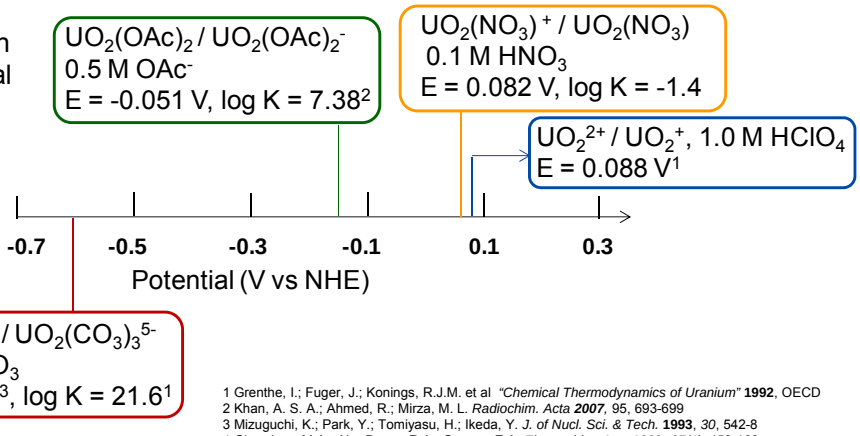
- Varying the length of alkyl chains has little effect on ECW.
- The branching of the alkyl chains ILs leads to a moderate increase of the ECW. The cathodic limit increased when the length of the side chain increased.
- Protic ILs tend to have the smallest ECWs
- Cyclic quaternary ammonium shows the largest ECW of ammonium ILs

Hagiwara, R.; et al *J. Electrochem. Soc.* **2003**, 150(12) D195-D19
Appetecchi, G.B.; et al *Electrochim. Acta* **2009**, *27*, 1325-1332

Finding the Right IL for An Electroplating

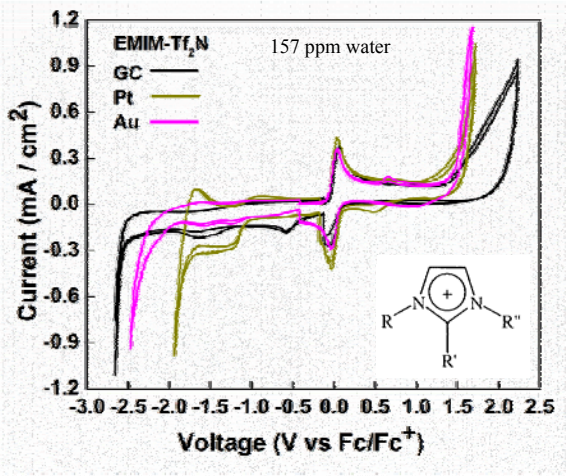
- Conventional ILs are weakly complexing and have low solubility for metals
  - Must identify a conventional IL with rapid plating kinetics to allow for process scale-up
- Task-specific ILs can be designed to complex with Pu to increase solubility
  - The stronger the complex, the higher the solubility
  - The stronger the complex, the harder it is to reduce!

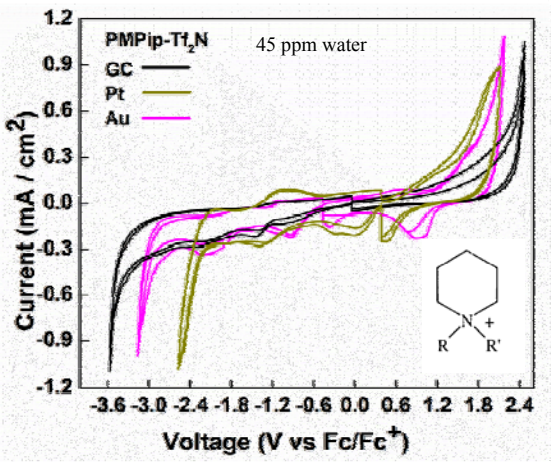
Effect of complexation on the formal redox potential for U(VI)/U(V)



1 Grenthe, I.; Fuger, J.; Konings, R.J.M. et al *"Chemical Thermodynamics of Uranium"* **1992**, OECD
2 Khan, A. S. A.; Ahmed, R.; Mirza, M. L. *Radiochim. Acta* ***2007***, 95, 693-699
3 Mizuguchi, K.; Park, Y.; Tomiyasu, H.; Ikeda, Y. *J. of Nucl. Sci. & Tech.* **1993**, *30*, 542-8
4 Ghandour, M.A.; Abo-Doma, R.A.; Gomaa, E.A. *Electrochim. Acta* **1982**, *27(1)*, 159-163

Choice of Working Electrode on ECW

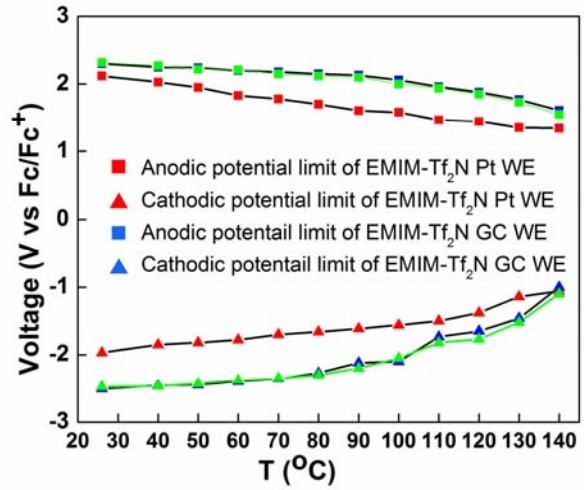


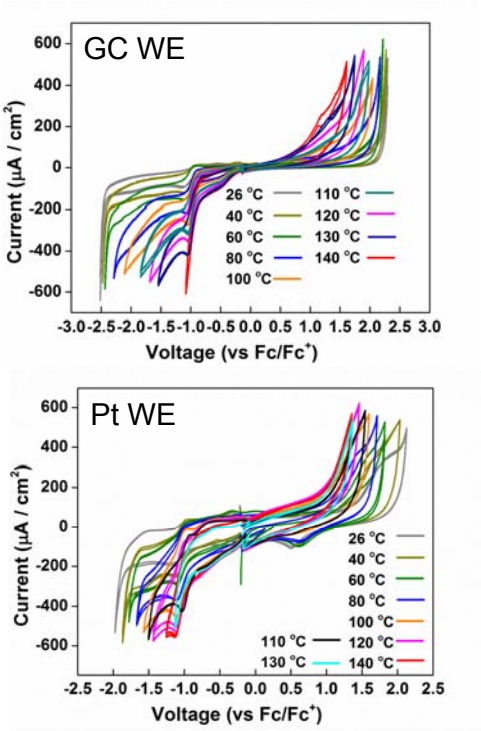


ECW (V)	EMIM-Tf_2N	PMPip-Tf_2N
GC	4.9	6.1
Pt	3.7	4.6
Au	4.1	5.3

Scan rate at 100 mV/sec

Effect of Temperature on ECW

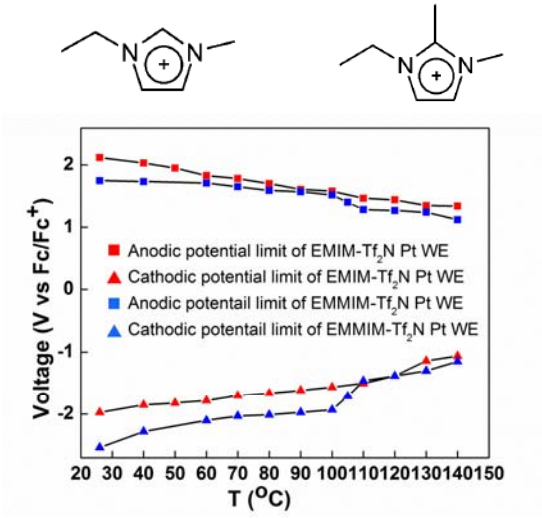




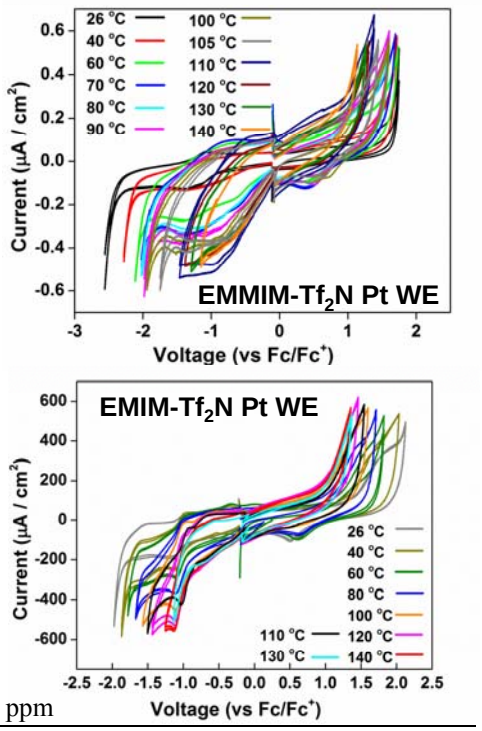
- **ECW shrinks with increasing temperature**
- **Data are reproducible**
- **GC WE provides wider ECW than Pt WE**

Scan rate: 25 mV /s; Water: 57 ppm

Effect of alkyl substitution on ECW



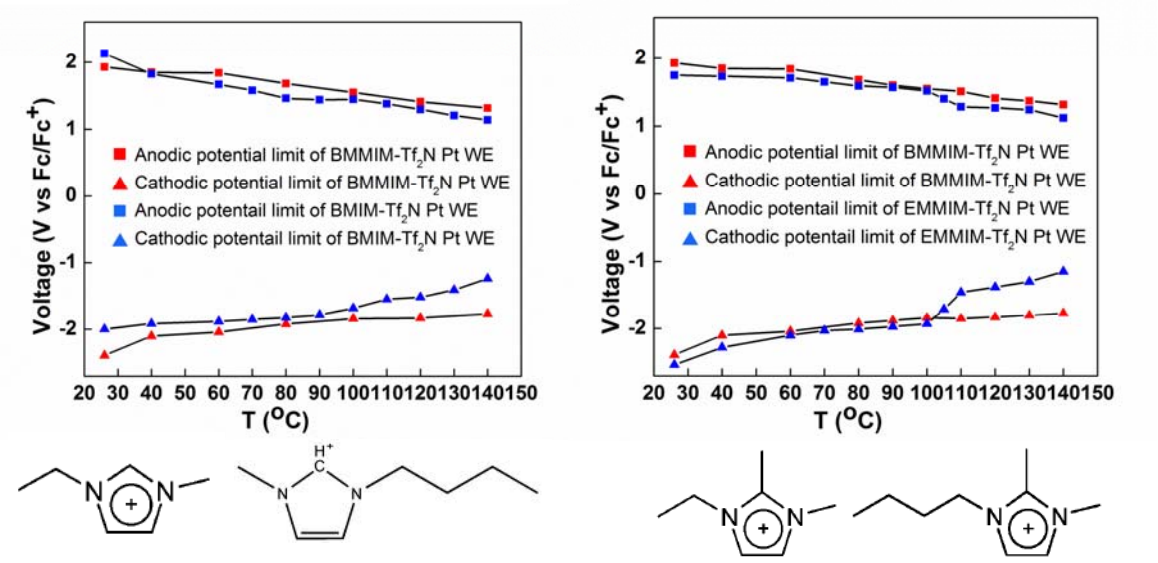
Substitution in the -2- position between the nitrogens gives slightly wider windows below 100 °C



Scan rate: 25 mV /s;
EMIM-Tf_2N: 57 ppm; EMMIM-Tf_2N: 58 ppm

Varing the Length of Alkyl Side Chain

Varying the length of alkyl side chains has little effect on ECW below 100 °C



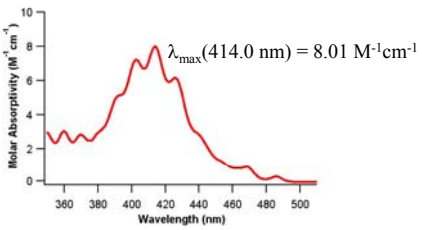
Scan rate: 25 mV /s;
EMMIM-Tf_2N 58 ppm; BMMIM-Tf_2N 29 ppm

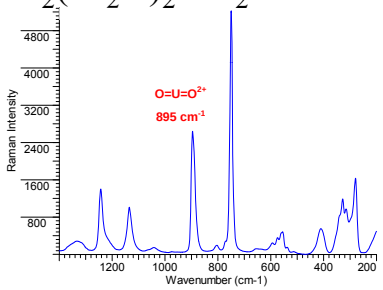
Preparation of Uranium-IL Solutions

$UO_2/U_3O_8/UO_3$
$UO_2(OH)_2$
UO_2CO_3
$UO_2(NO_3)_2$
UO_2Cl_2

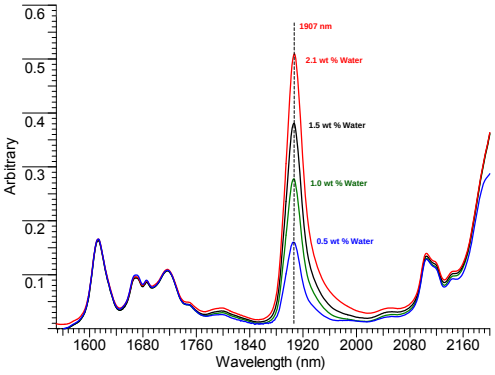
$$+ \text{ 1-2 M } HTf_2N \xrightarrow[\text{2. Rotovap}]{\text{1. Heat}} UO_2(Tf_2N)_2 \cdot nH_2O + IL$$

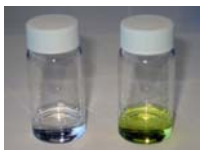
UV-vis of UO_2^{2+} in 1 M HTf_2N





Water content of ILs characterized by Karl-Fischer Titrations and NIR absorbance



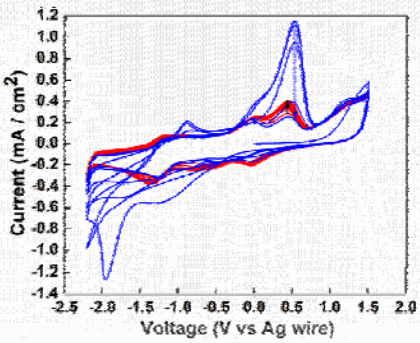


40 mM U(VI) in [PMPip][Tf_2N]

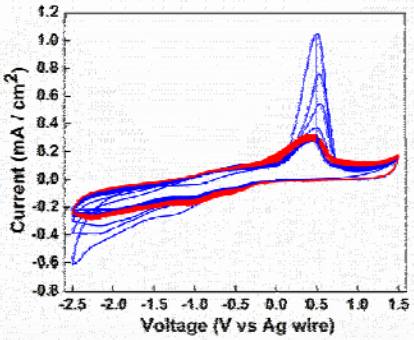
Solutions can also be made by direct dissolution into the IL followed by water removal

Echem of $UO_2(Tf_2N)_2$ in PMPip-Tf_2N at High Temperature

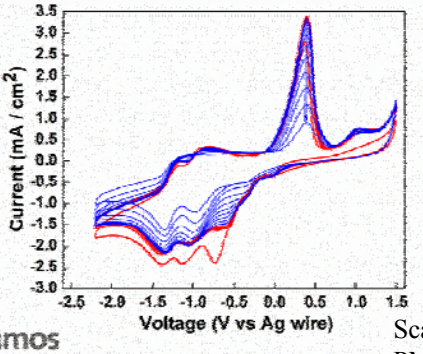
RT
Pt WE



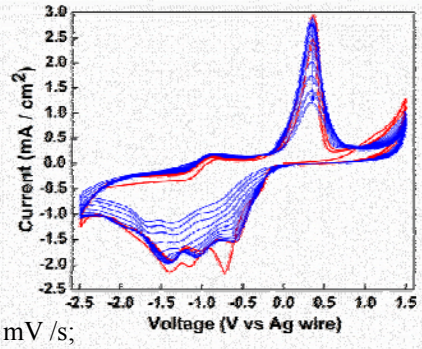
RT
GC WE



80 °C
Pt WE



80 °C
GC WE

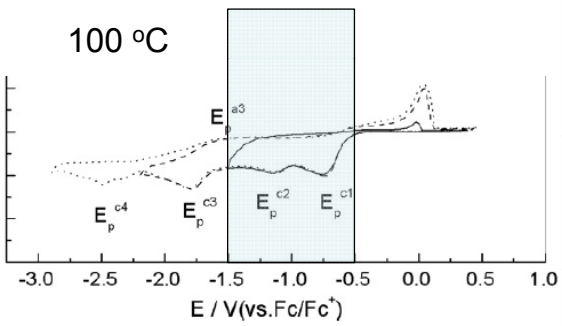


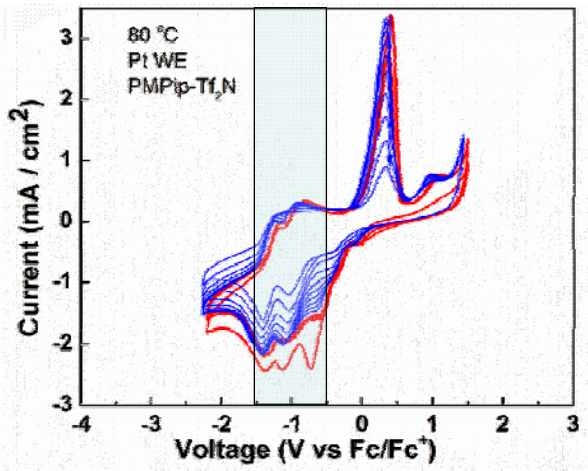
Scan rate: 100 mV /s;
PMPip-Tf_2N: 160 ppm

Comparison to Literature

Rao, C.J. et al, *J. Nucl. Mat.* **2011** 408, 25-29.

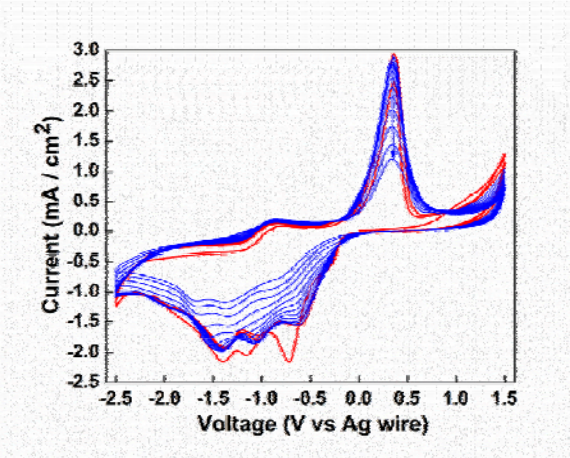
100 °C

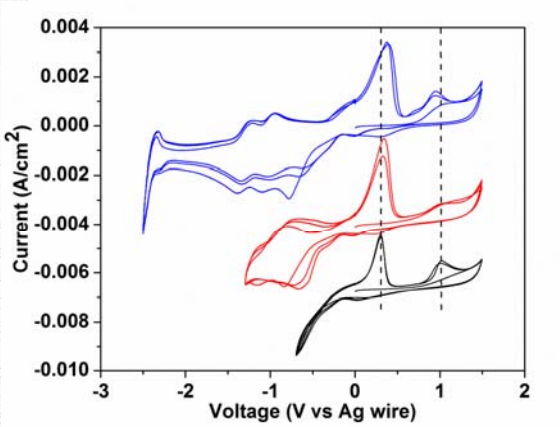




- Rao et al dissolved UO_2 into HTf_2N (aq) to make $U(Tf_2N)_4$ as the starting material
- E^{c1}_p and E^{c2}_p assigned to the U(IV/III) couple of different solution complexes
- E^{c3}_p was unassigned and E^{c4}_p assigned to reduction of uranium into metallic form
- No deposition observed at -1.9 V(E^{c3}_p)

$UO_2(Tf_2N)_2$ in PMPip-Tf_2N

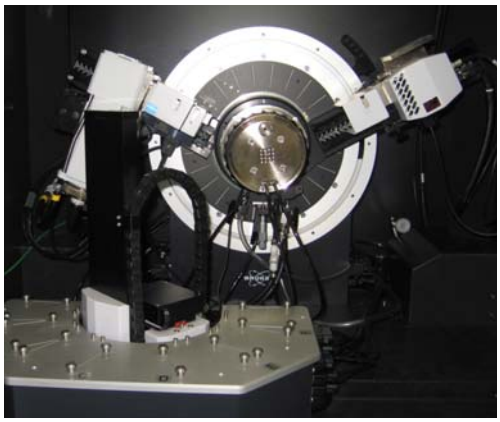


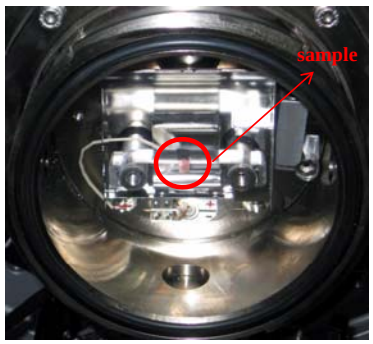


40 mM du-Tf_2N in PMPip-Tf_2N, Pt working electrode, Ag wire reference electrode, Pt gauge counter electrode, 80 ^{0}C
Right: scan from 1.5 V to -0.7, -1.3 and -2.5 V

Scan rate: 100 mV /s; PMPip-Tf_2N: 160 ppm

Sample Annealing

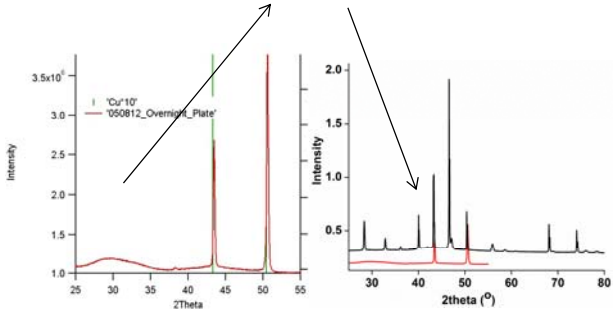




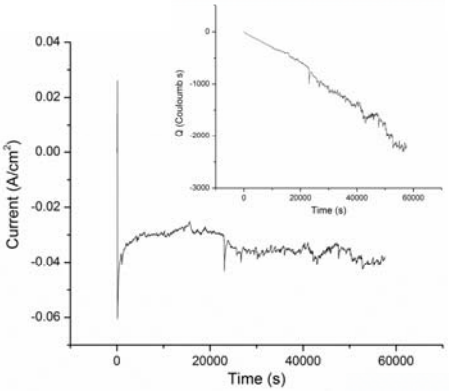
In situ measurement allows for tracking of annealing process. Samples cooled to room T for final measurement.

Bruker D8 Advance Diffractometer
High Temperature Chamber
- PtRh heating stage, up to 1600°C
- Vacuum capability
- Gas purge/humidity control

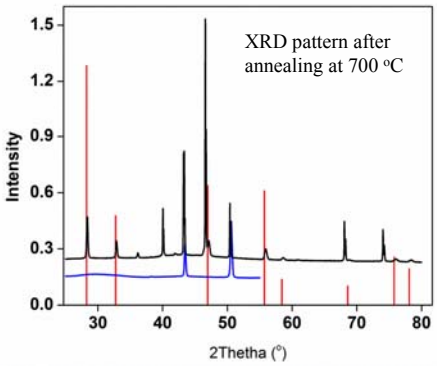
Anneal in UHP Ar at 700°C



$UO_2(Tf_2N)_2$ in PMPip-Tf_2N

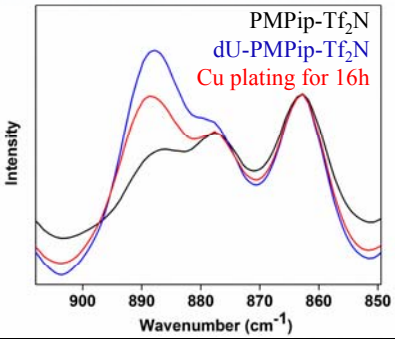


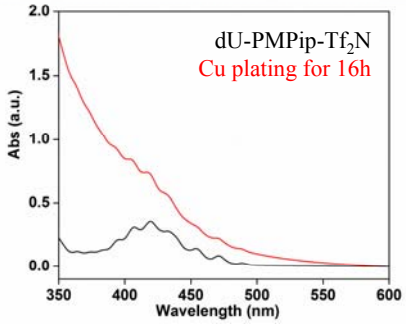
Electroplated ~15 mg UO_2, Faradaic efficiency ~63%



40 mM du-Tf_2N in PMPip-Tf_2N, electrolysis at -2.8 V for 16 h (80 ^{0}C)

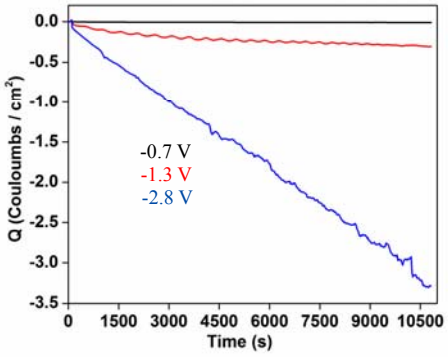
Cu working electrode, Ag wire reference electrode, Pt gauge counter electrode

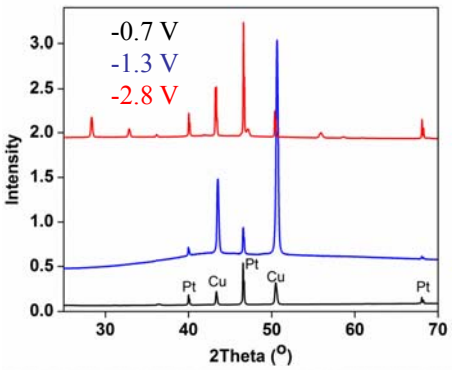




PMPip-Tf_2N Electroplating Comparison

Cu electroplating in du-PMPip-Tf_2N for 3 hours



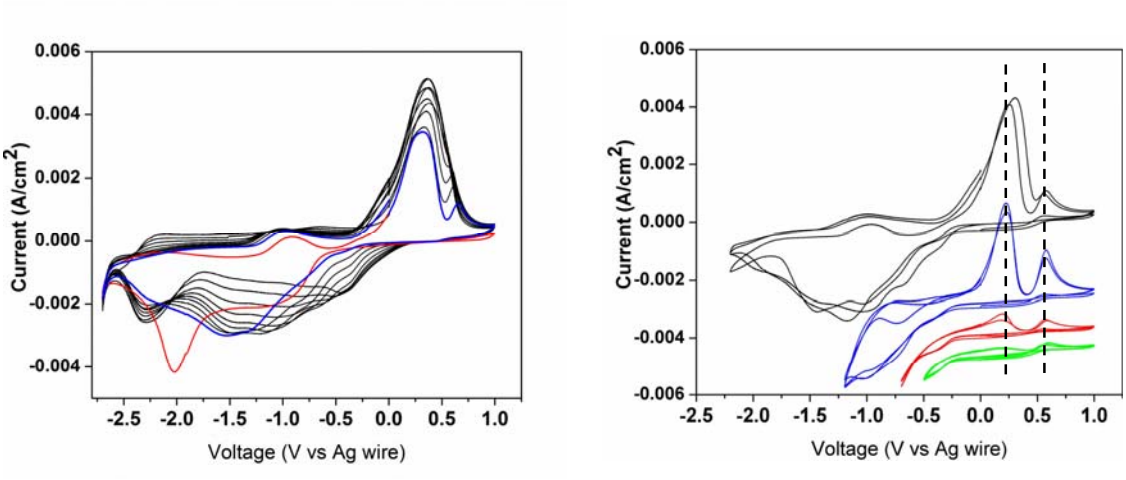


-0.7 V

-1.3 V

-2.8 V

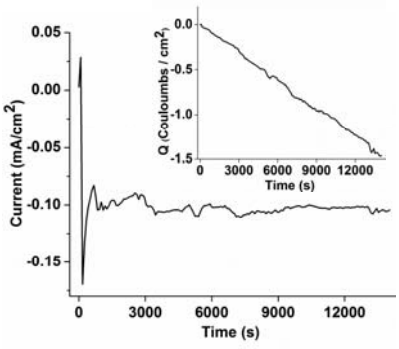
$UO_2(Tf_2N)_2$ in EMIM-Tf_2N



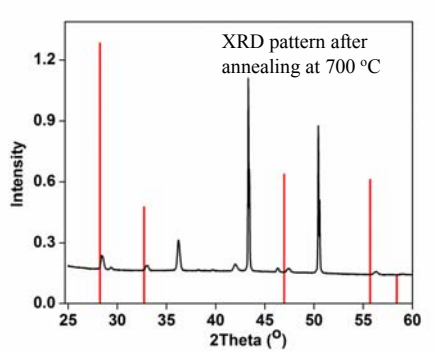
40 mM du-Tf_2N in EMIM-Tf_2N, GC working electrode, Ag wire reference electrode, Pt gauge counter electrode, 80 ^{0}C
Right: scan from 1.0 V to -0.5, -0.7, -1.2 and -2.2 V

Scan rate: 100 mV /s; EMIM-Tf_2N 185 ppm

$UO_2(Tf_2N)_2$ in EMIM-Tf_2N

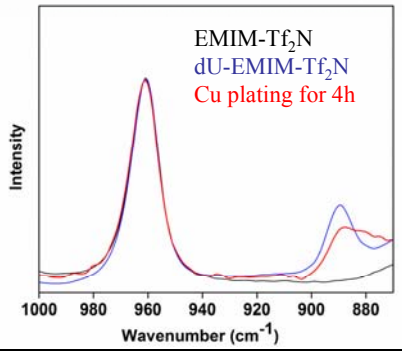


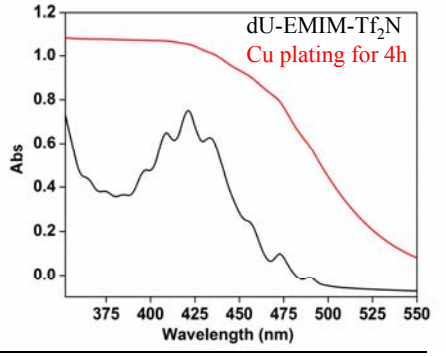
Electroplated ~10 mg UO_2, Faradaic efficiency ~69%



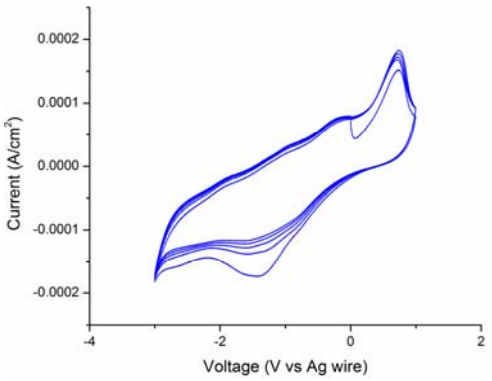
40 mM du-Tf_2N in EMIM-Tf_2N, electrolysis at -2.8 V for 4 h (80 ^{0}C)

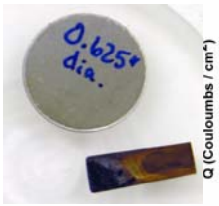
Cu working electrode, Ag wire reference electrode, Pt gauge counter electrode

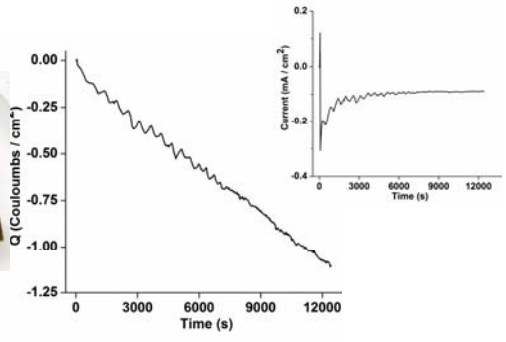




$UO_2(Tf_2N)_2$ in $P_{6,6,6,14}$-Tf_2N

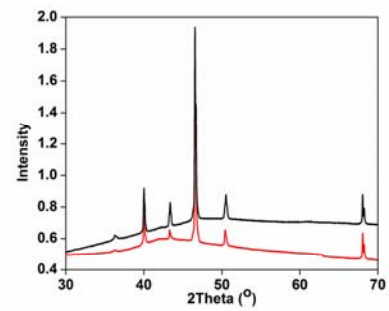


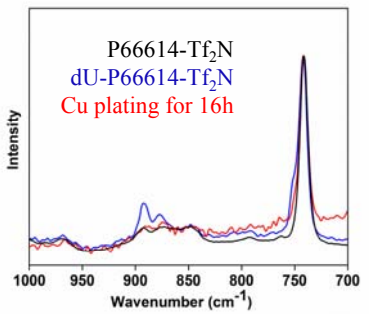




40 mM du-Tf_2N in $P_{6,6,6,14}$-Tf_2N, electrolysis at -2.8 V for 16 h (80 ^{0}C)

Cu working electrode, Ag wire reference electrode, Pt gauge counter electrode





Conclusions

- The choice of working electrode material can also dramatically impact the ECW and cathodic reduction limit. Pt < Au < GC
- Increasing the temperature decreases both the ECW and the cathodic reduction limit. (6.1 V at RT to 4.4 V at 90°C for [PMPip][Tf_2N])
- Milligram quantities of UO_2 was successfully electroplated from [EMIM][Tf_2N], [PMPip][Tf_2N], and [P_{66614}][Tf_2N] at 80°C.
- Solution electrochemistry is highly complex, with multiple reduction and oxidation peaks. Still unraveling this chemistry.
- Different plating voltages were examined for [PMPip][Tf_2N]. At -0.7 V, no measurable precipitation occurred. At -1.3 V visible precipitate, XRD inconclusive. At -2.8V UO_2 was depositied and characterized by XRD.
- Faradaic efficiencies of 68% and 63% were estimated for [EMIM][Tf_2N] and [PMPip][Tf_2N]. Deposition rates were constant and deposition kinetics are faster in [EMIM][Tf_2N] (10 mg UO_2 in 4 hrs) compared to [PMPip][Tf_2N] (15 mg in 16 hours).

Successfully demonstrated UO_2 deposition from conventional ionic liquids!

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