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Title: Metal Electrodeposition and Electron Transfer Studies of Uranium Compounds in Room Temperature Ionic Liquids

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Metal Electrodeposition and Electron Transfer Studies of Uranium Compounds in Room Temperature Ionic Liquids

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Room temperature ionic liquids (RTIL's) comprised of 1,3-dialkylimidazolium or quaternary ammonium cations and one of several anions such as PF_6^-, BF_4^-, or $^-N(SO_2CF_3)_2$, represent a class of solvents that possess great potential for use in applications employing electrochemical procedures. Part of the intrigue with RTIL's stems from some of their inherent solvent properties including negligible vapor pressure, good conductivity, high chemical and thermal stability, and non-flammability. Additionally, a substantial number of RTIL's can be envisioned simply by combining different cation and anion pairs, thereby making them attractive for specific application needs. We are interested in learning more about the possible use of RTIL's within the nuclear industry. In this regard our research team has been exploring the electron transfer behavior of simple metal ions in addition to coordination and organometallic complexes in these novel solvents. Results from our research have also provided us with insight into the bonding interactions between our current anion of choice, bis(trifluoromethylsulfonyl)imide ≡ NTf_2, and open coordination sites on actinide and transition metal fragments.

This presentation will focus on recent results in two areas: the electrodeposition of electropositive metal ions from RTIL solutions and the electron transfer behavior for several uranium complexes. Details concerning the cathodic electrodeposition and anodic stripping of alkali metals (Na, K) from various working electrode surfaces (Pt, Au, W, Glassy Carbon) will be discussed. Figure 1 displays typical behavior for the electrodeposition of potassium metal from an RTIL containing potassium ions produced through the reaction of KH with $H[NTf_2]$. Our efforts with other metal ions, including our results to date with uranium electrodeposition, will be covered during the presentation.

The electron transfer behavior for a number of uranium complexes have been studied with various electrochemical methods including cyclic and square-wave voltammetry, chronoamperometry, and bulk coulometry. Results from these studies will be presented to show the general electron transfer behavior of metal complexes in the RTIL's. As an example, Figure 2 shows the difference in chemical stability of an electrogenerated U(V) anion for two uranyl ($U(VI)O_2^{2+}$) complexes due to the difference in ancillary ligands about the uranyl moiety. Figure 2a shows a cyclic voltammogram (CV) for the U(VI)/U(V) couple of a uranyl complex containing a multi-dentate chelating nitrogen/oxygen ligand (inset in figure). The couple is both chemically and electrochemically reversible. The CV in Figure 2b is that of $[UO_2Cl_4]^{2-}$ in which the electrogenerated U(V) derivative is unstable yielding a chemically irreversible wave. For the compound giving rise to the CV in Figure 2a its electrochemical behavior in a conventional non-aqueous electrolyte medium is very similar to that obtained in the RTIL. While this result does not illustrate a distinct advantage for employing the RTIL solvent in this particular case, we believe it effectively demonstrates the ability of the RTIL to be utilized as a solvent/electrolyte medium for detailed electrochemical studies without severe limitations.

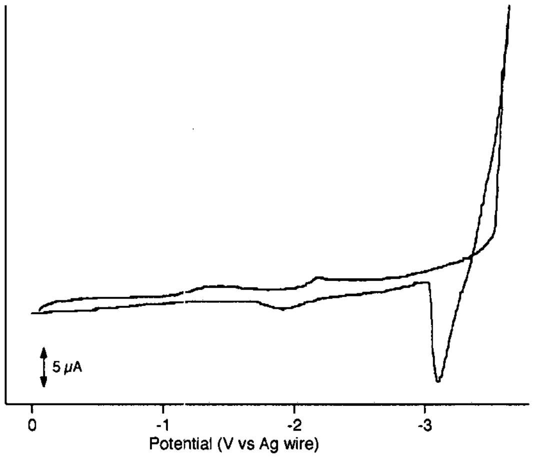

Figure 1. Cyclic voltammogram (0.1 V/s, 1mm Pt disk) of K metal electroplating and stripping from a solution of KH and $H[NTf_2]$ in $[(CH_3)_2N(C_3H_7)(C_3H_6)][NTf_2]$.

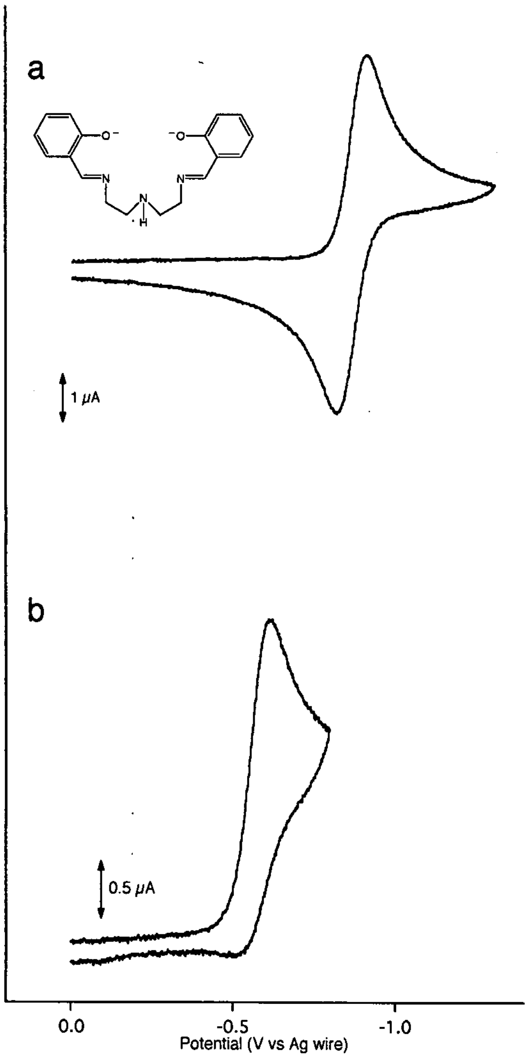

Figure 2. Cyclic voltammograms (0.1 V/s, 1.5 mm GC disk) of (a) UO_2(saldiene) and (b) $[UO_2Cl_4]^{2-}$ in [ethylmethylimidazolium][NTf_2].

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Outline

I. Introduction

II. Electrochemistry of Uranium Compounds

- U(VI): UO_2^{2+}
- U(IV): UCl_6^{2-}

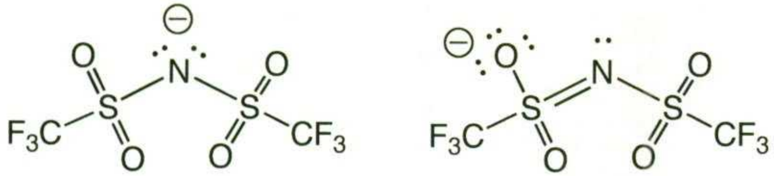
III. Electrodeposition of Electropositive Metals

- Na, K, Li, Al

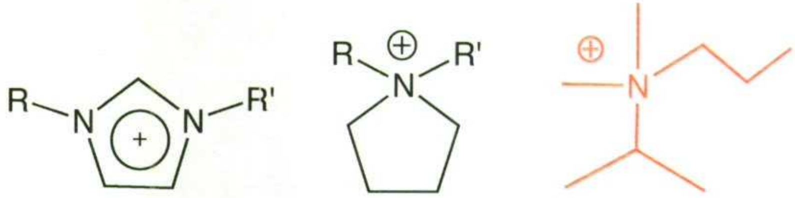
IV. Conclusion/Future Directions

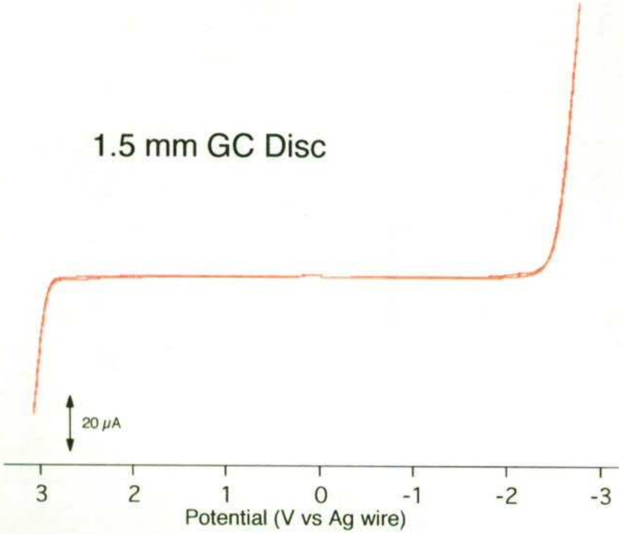
Room Temperature Ionic Liquids

- Main RTIL's being studied contain 1,3-dialkylimidazolium, N,N-dialkylpyrrolidinium and acyclic ammonium cations with bis(trifluoromethylsulfonyl)imide, $^{-}N(SO_2CF_3)_2$, as an anion

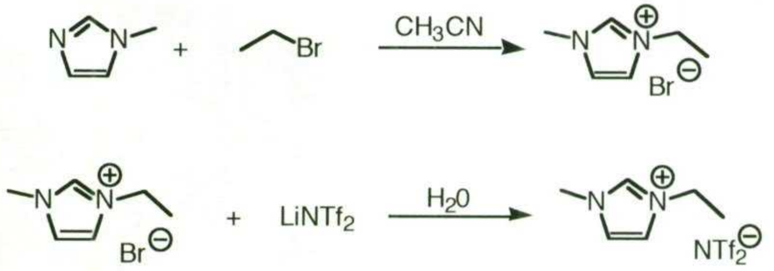


≡ NTf_2



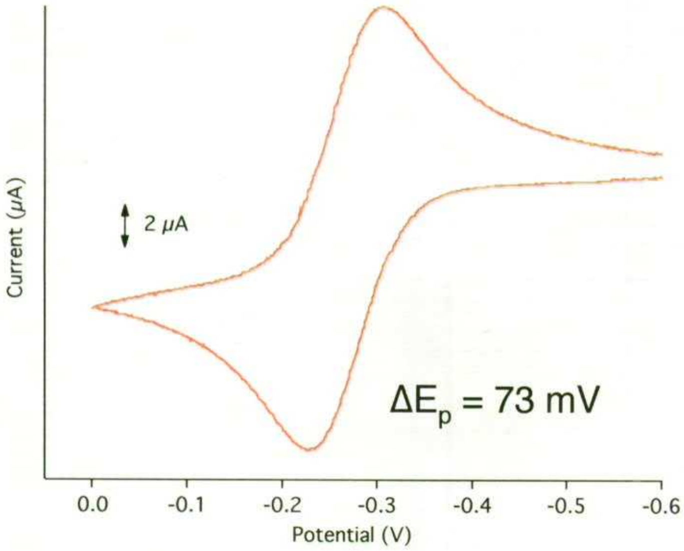


General Synthetic Scheme

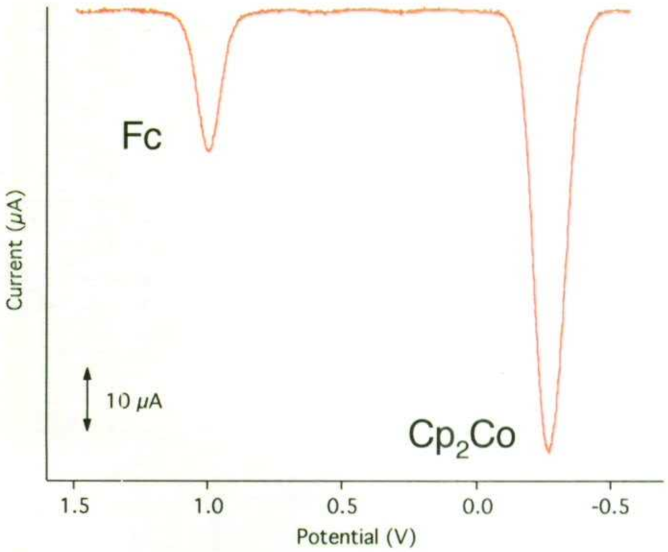


Electrochemistry in $^{-}NTf_2$ Ionic Liquids

Cp_2Co in $[EMI][NTf_2]$
100 mV/s 2mm Pt disc

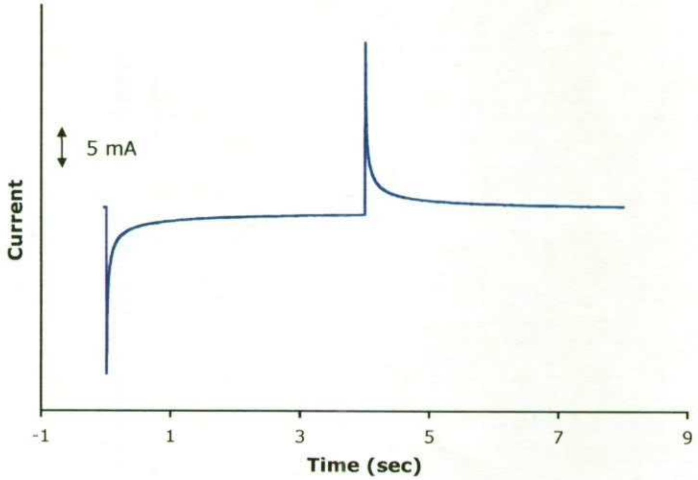


Cp_2Co/Cp_2Co^+ at -1.27 vs Fc/Fc^+



Cottrell Equation:

$i = nFACD^{1/2}/t^{1/2}\pi^{1/2}$



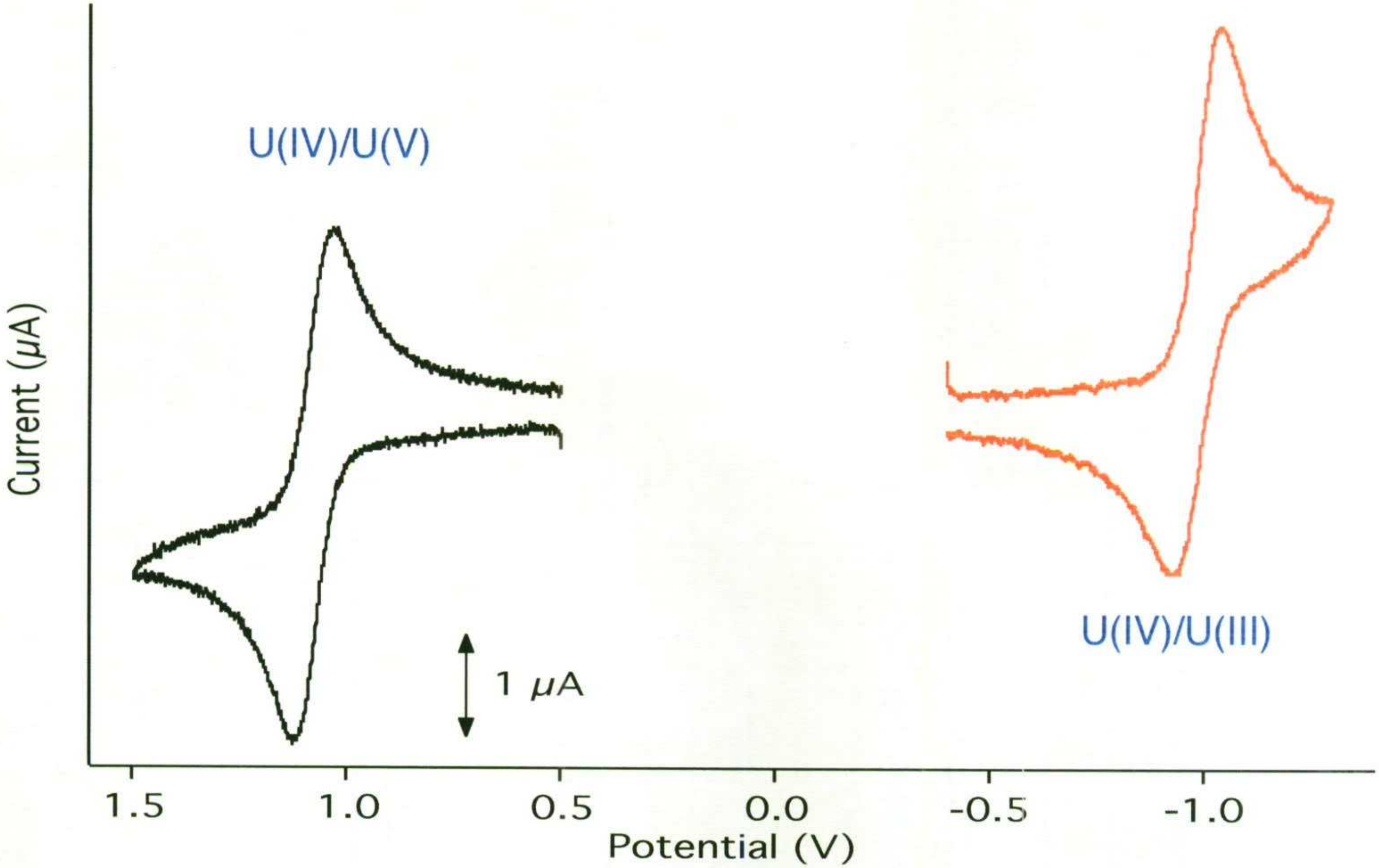
Diffusion coefficients for Fc:

MeCN/0.1 M $[TBA][PF_6]$ = 1.19×10^{-5} cm^2/s

Neat $[EMI][NTf_2]$ = 1.93×10^{-7} cm^2/s

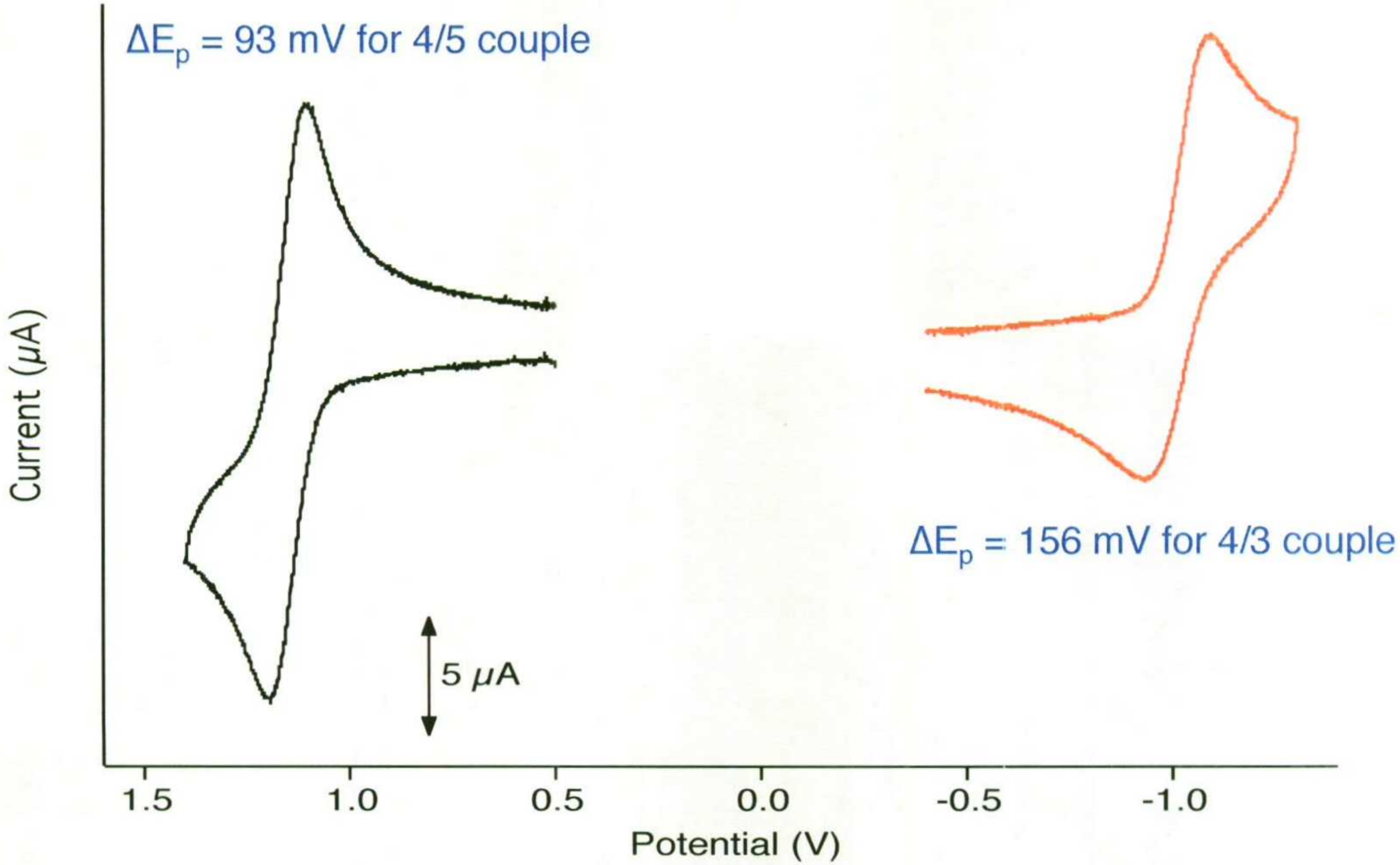
Voltammetry of $[UCl_6][EMI]_2$ in $[EMI][NTf_2]$

50 mV/s, 1.5 mm GC disk



Voltammetry of $[UCl_6][EMI]_2$ in $[EMI][NTf_2]$

1000 mV/s, 1.5 mm GC disk



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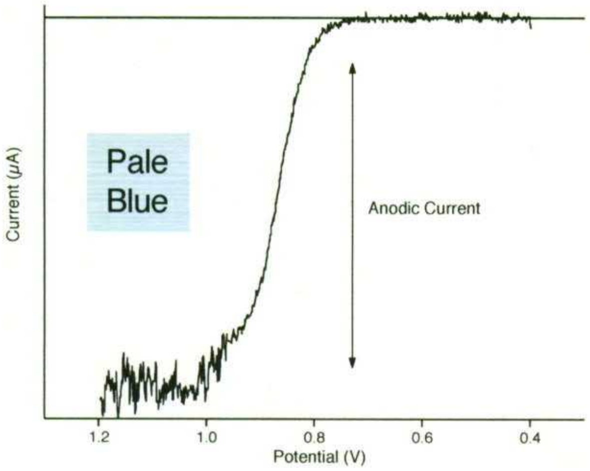
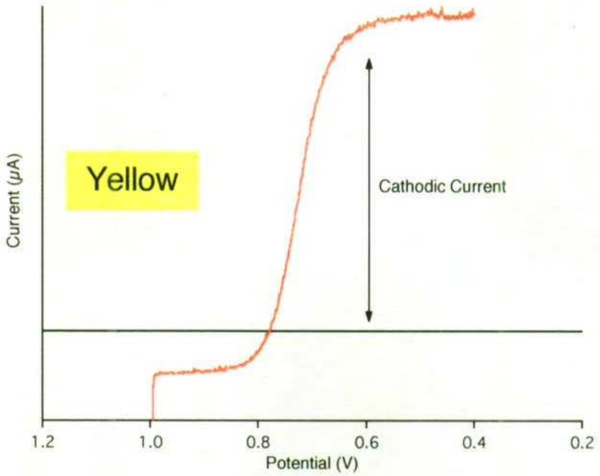
Bulk Electrolysis of $[UCl_6][EMI]_2$ in $[EMI][NTf_2]$

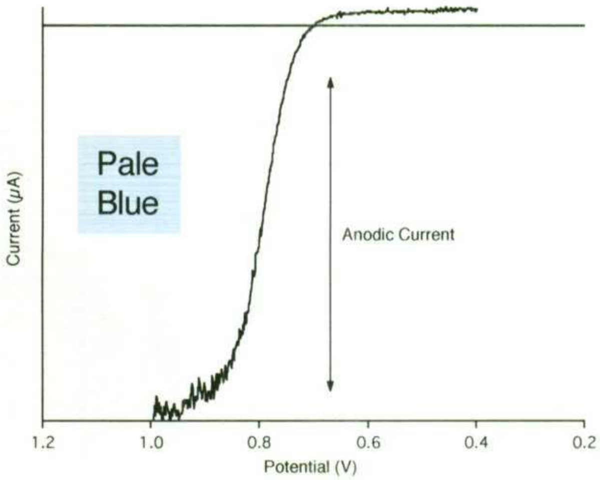
Stirred Solution Voltammograms: 1.5 mm GC disc, 3 mV/s



U(IV)



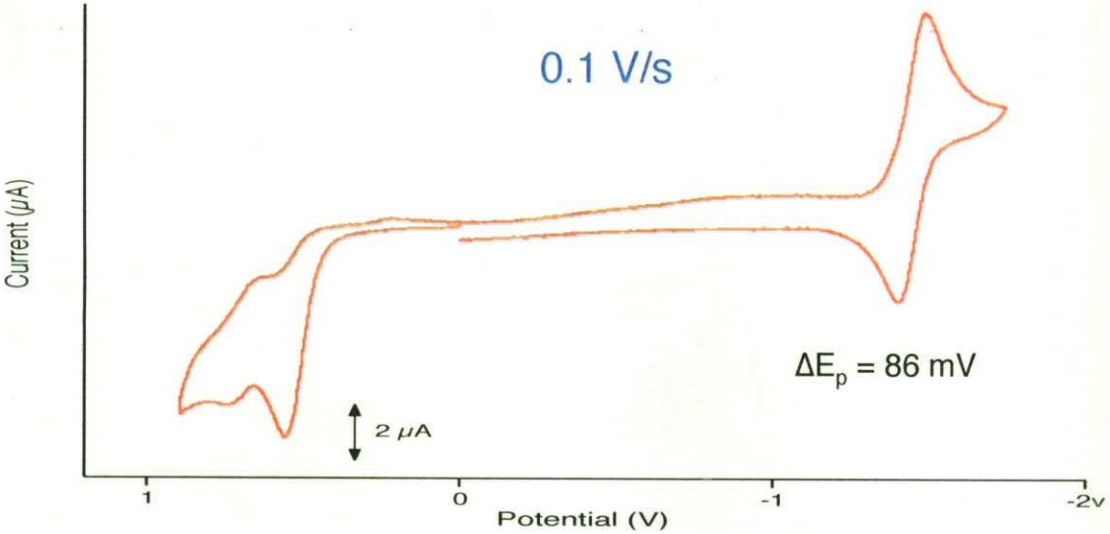
U(V)

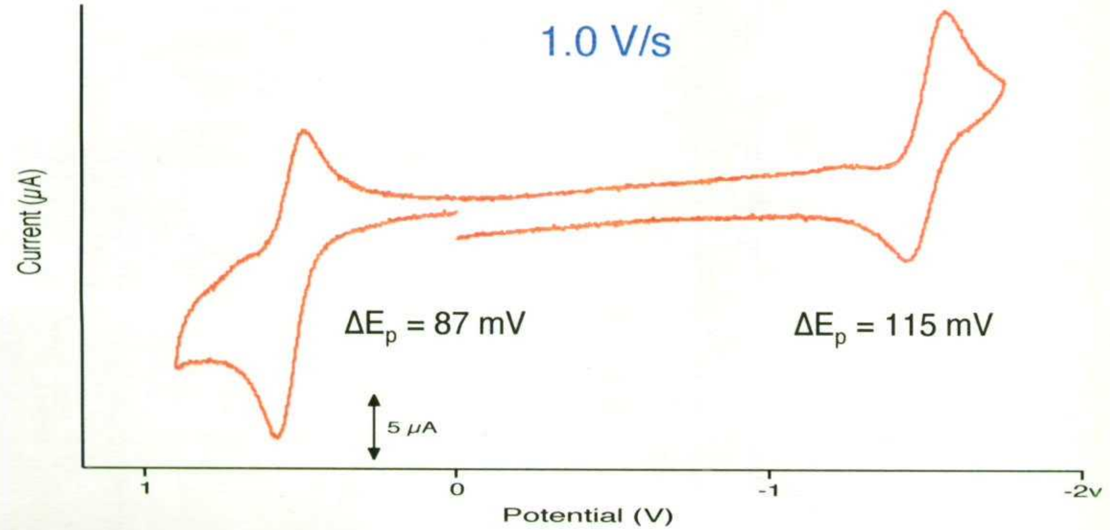


U(IV)

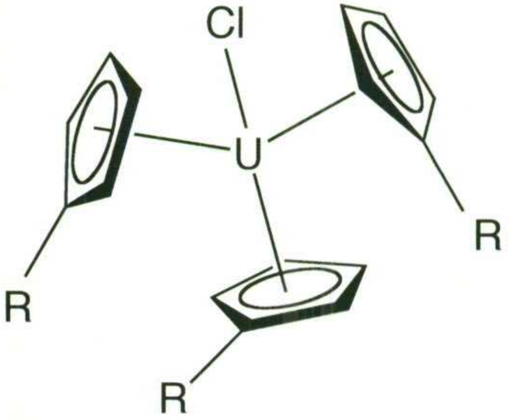
- E_{app} during bulk was set 300 mV positive of $E_{1/2}$ for U(IV)/U(V) couple
- $[U(V)Cl_6]^-$ is stable in $[EMI][NTf_2]$ on the bulk electrolysis time scale
- Coulometry was 94% efficient for a 1-electron oxidation process

Voltammetry of (ipr-Cp)$_3$UCl in Acetonitrile



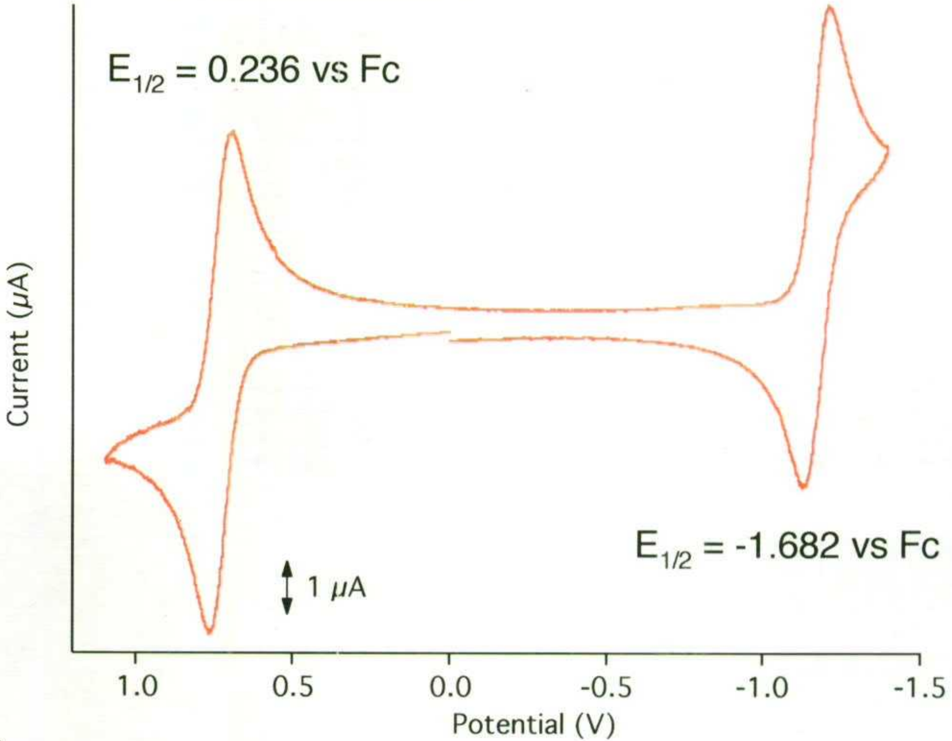


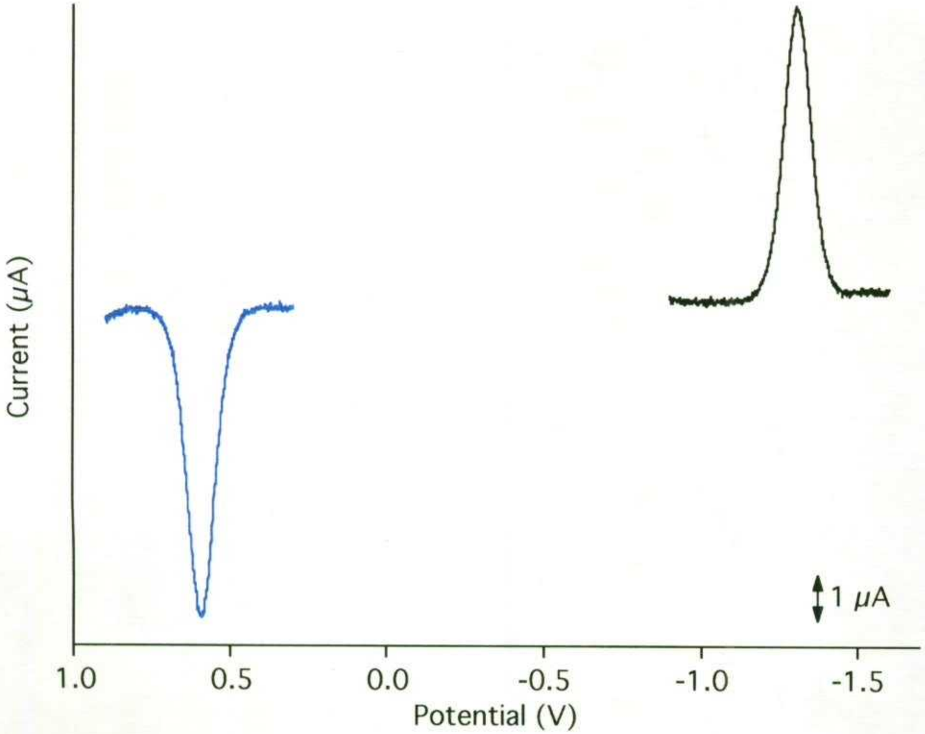
0.1 M [TBA][PF$_6$] in MeCN
1.5 mm GC disk



Voltammetry of (ipr-Cp)$_3$UCl in [EMI][NTf$_2$]

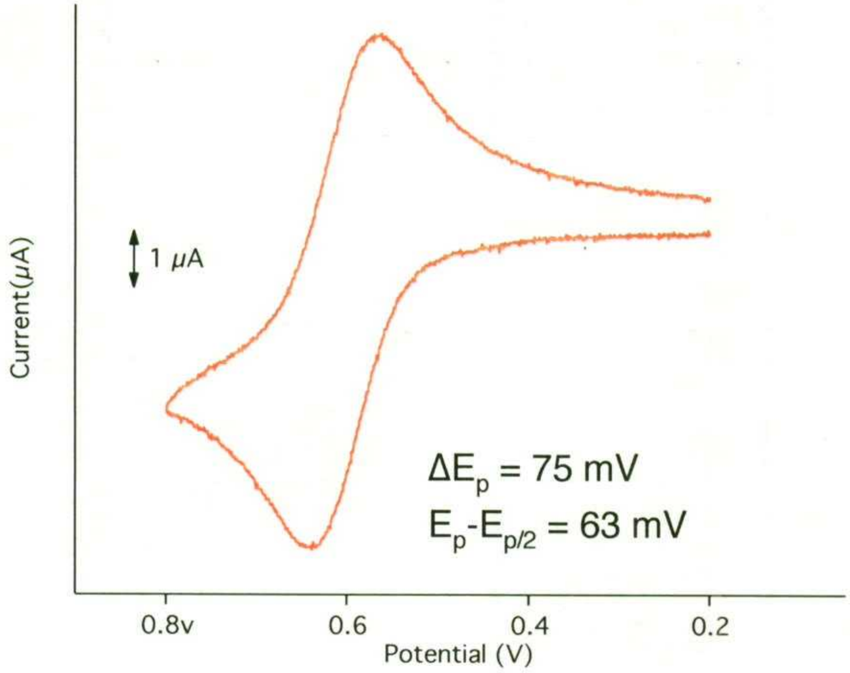
0.1 V/s
2 mm Pt disk
$\Delta E_{1/2}$ = 1.918 V

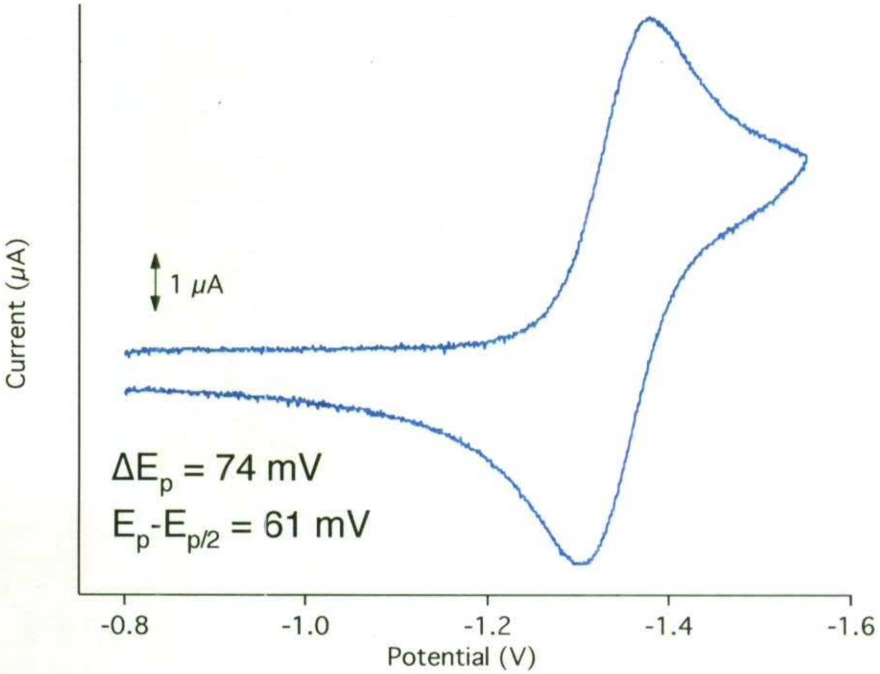




100 Hz
1 mm Pt disk
Peak current and $W_{1/2}$ consistent between two waves

Voltammetry of (ipr-Cp)$_3$UCl in [EMI][NTf$_2$] at 2 V/s

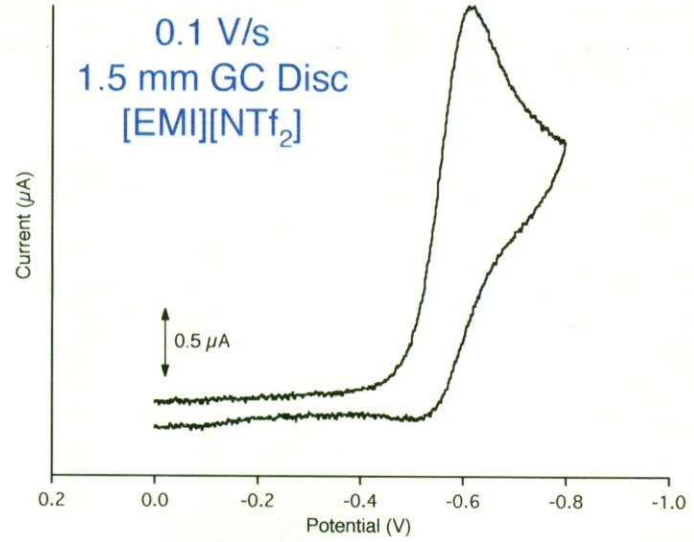


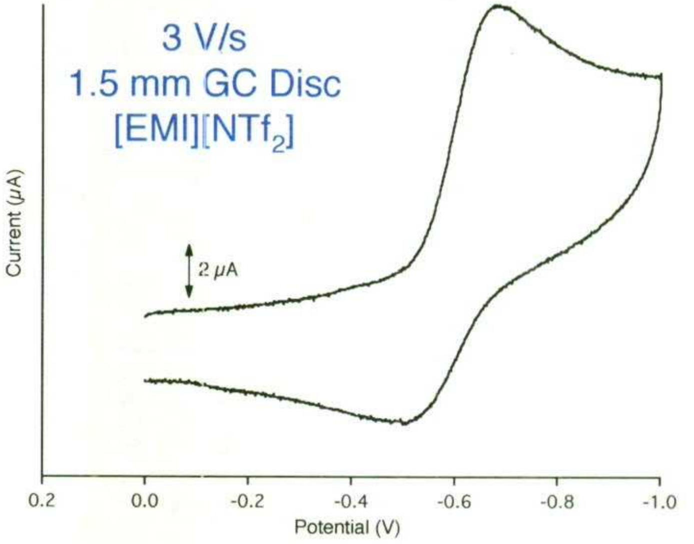


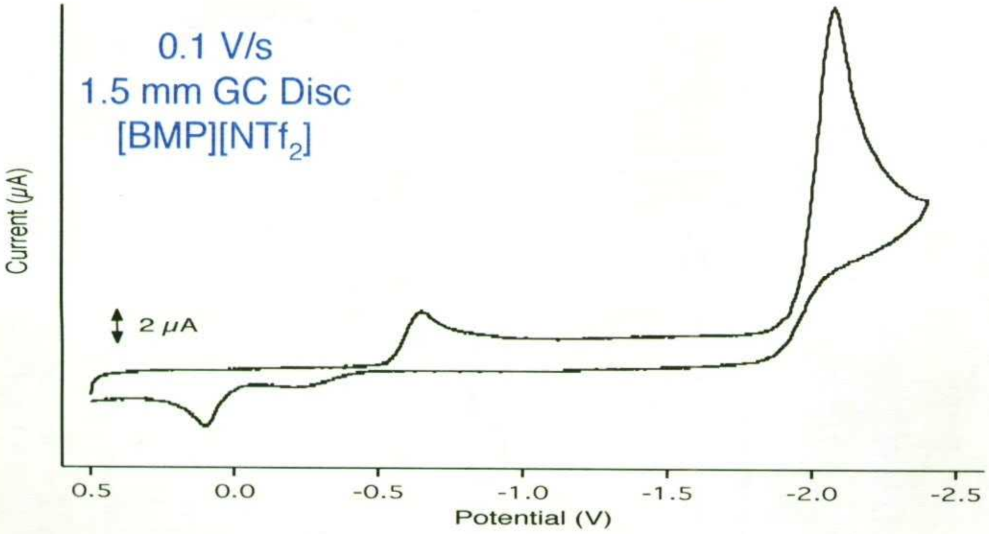
- Chronoamperomograms give D = 2.25 x 10^{-7} cm^2/s
- Theory predicts $i_{rev}(2\tau)/I_{fwd}(\tau)$ = 0.293 for full chemical reversibility
- Experimental data give 0.275 at τ = 3s for 5/4 couple

and 0.146 at τ = 3s for 4/3 couple

Voltammetry of $[UO_2Cl_4][EMI]_2$ in $[Cat][NTf_2]$







- Chemically irreversible U(VI/V) couple
- No additional reduction processes observed in $EMINTf_2$
- High-current reduction process at more cathodic potentials in $BMPNTf_2$

Production of $U(V)O_2^+$ Complexes in Non-Aqueous Solution

$UO_2(L)_2$dmso: Tomiyasu and Ikeda et al., *J. Alloys Compd.*, **1998**, *271-273*, 163

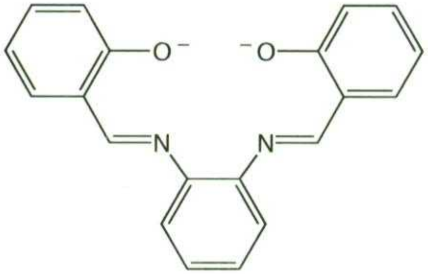
- L = trifluoroacetylacetonate, hexafluoroacetylacetonate
- Chemically reversible reduction to $[U(V)O_2(L)_2dmso]^-$ species in dmso/$TBAClO_4$

$UO_2(OPPh_3)_4(OTf)_n$: Berthet et al., *Angew. Chem. Int. Ed.*, **2003**, *42*, 1952

- U(V) species characterized by single crystal X-ray diffraction
- U=O bond lengths increase by ca. 0.06 Å

UO_2(saloph)L: Ikeda et al., *Inorg.*, **2003**, *42*, 3396 and 1031

- L = dimethyl sulfoxide, *N,N*-dimethylformamide
- Electrochemical and spectroscopic characterization of U(V) species
- IR spectroelectrochemical results display 125 cm^{-1} shift to lower energy (895 to 770 cm^{-1}) for the U(V) species

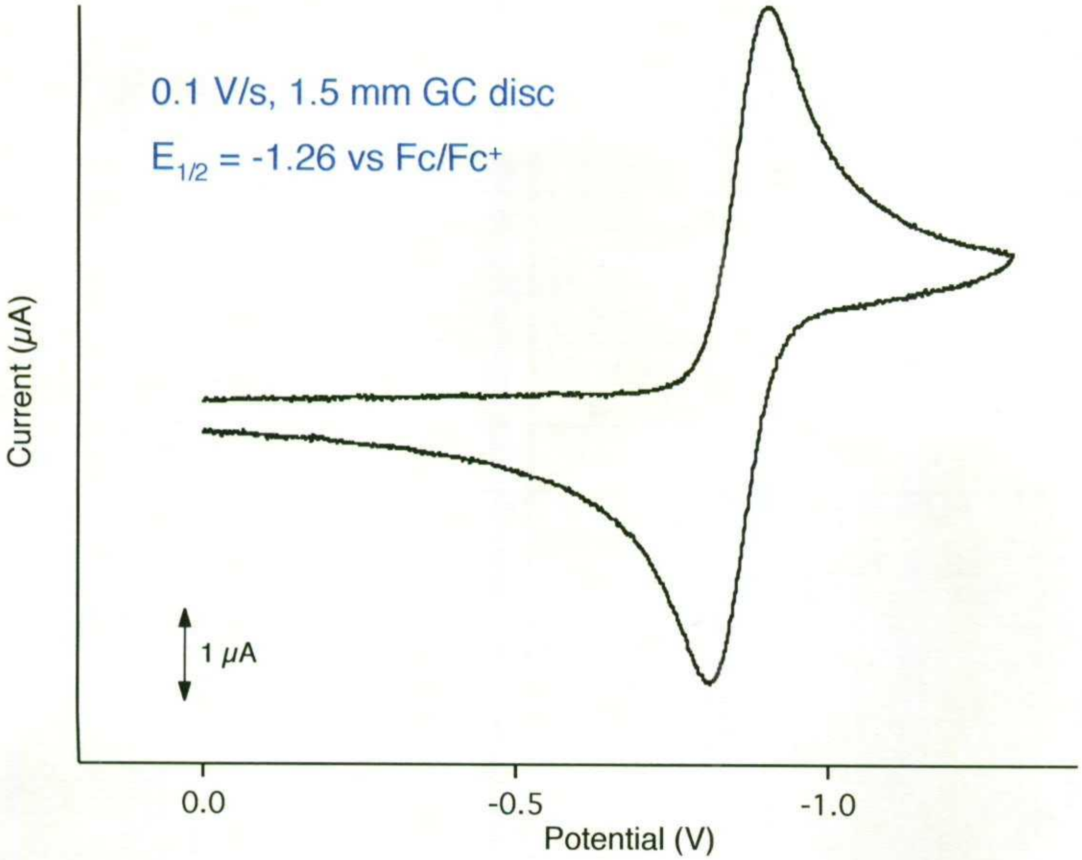


Saloph = *N,N*-disalicylidene-*o*-phenylenediaminate

UO_2(saldiene): Currently under investigation in our Laboratory

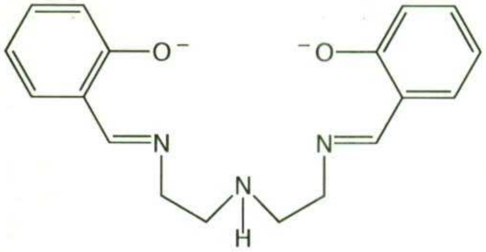
- Saldiene is a five coordinate (N_3,O_2) multi-dentate ligand

Voltammetry of UO_2(saldiene) in [EMI][NTf_2]



0.1 V/s, 1.5 mm GC disc

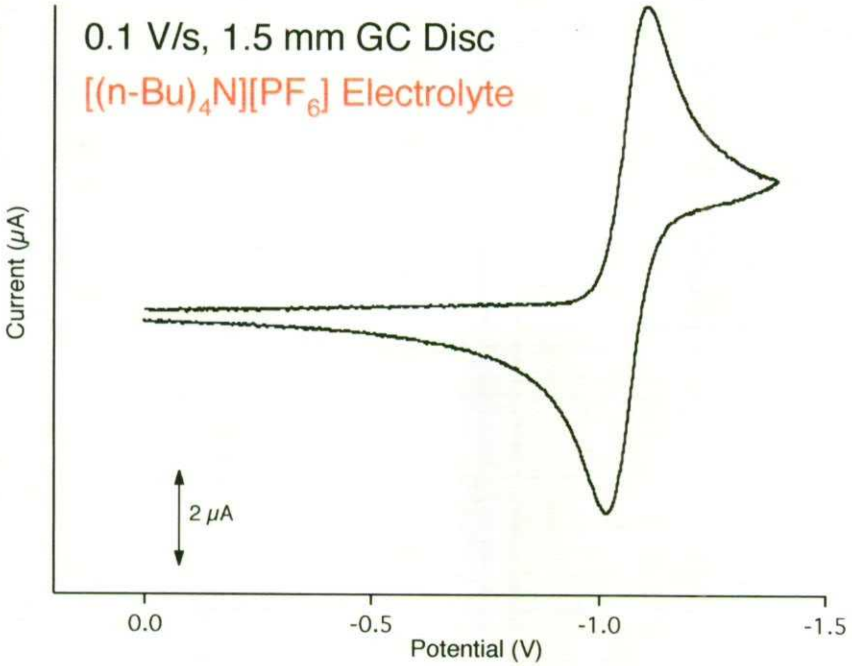
$E_{1/2}$ = -1.26 vs Fc/Fc$^+$

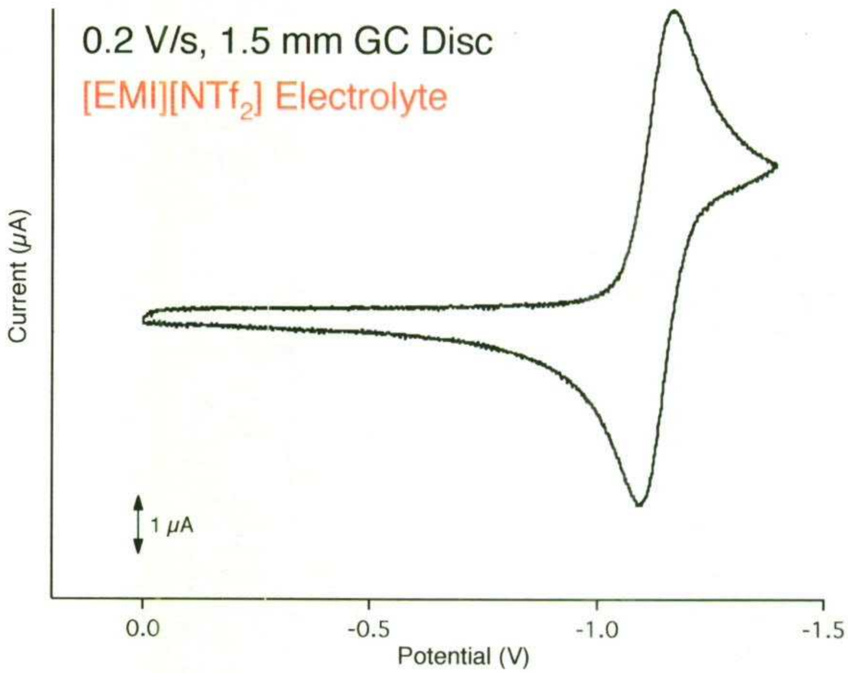


N,N´-bissalicylidene-1,5-diamino-3-azapentane

- Voltammetry in [EMI][NTf_2] gives chemically and electrochemically reversible reduction, U(VI)/U(V) couple

Electrochemistry of UO_2(saldiene) in MeCN



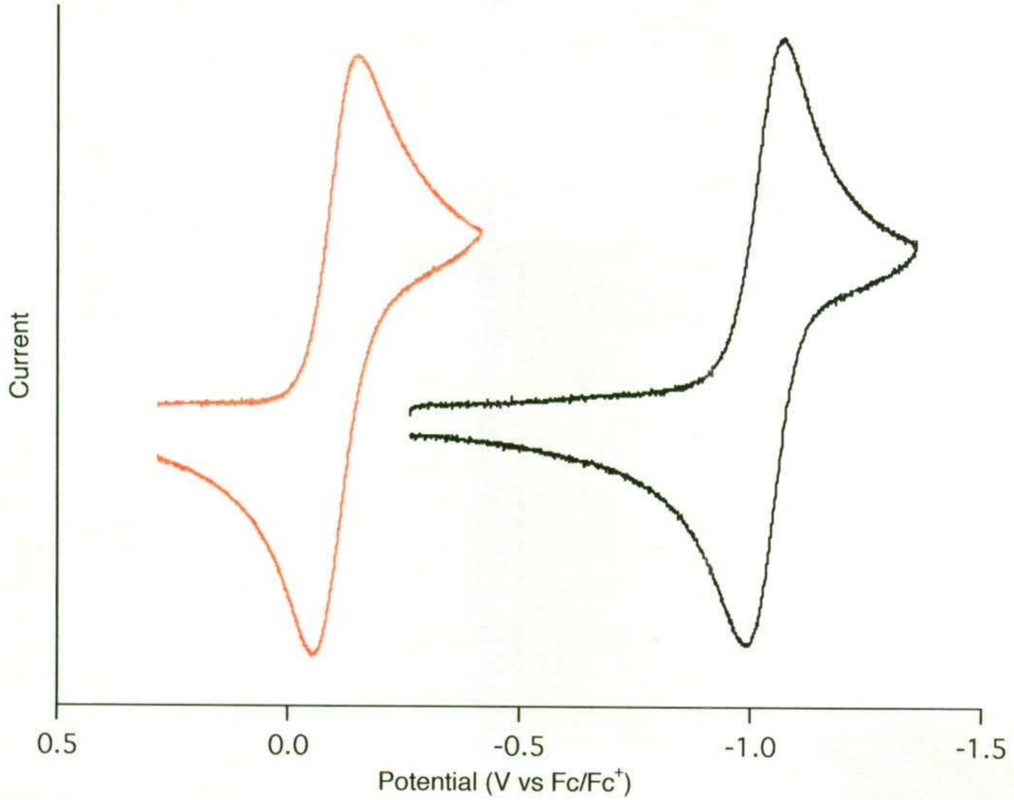


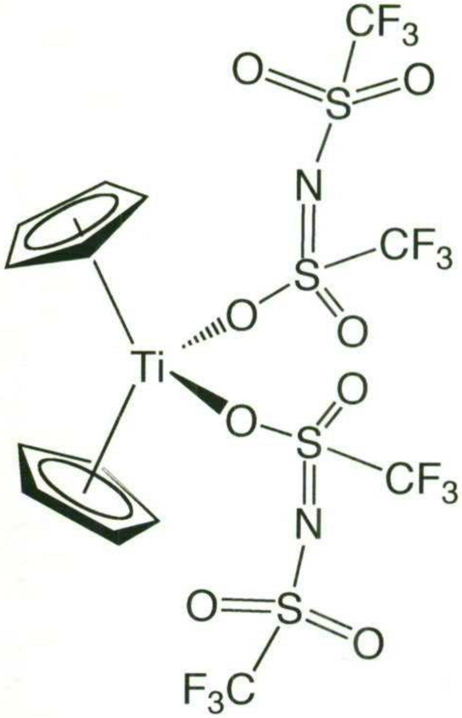
- Voltammetric behavior in MeCN with either $EMINTf_2$ or $TBAPF_6$ as supporting electrolyte mimics behavior in neat $EMINTf_2$

- Bulk electrolysis experiment with $EMINTf_2$ as electrolyte gives quantitative conversion to U(V) and subsequent reoxidation to the U(VI) species

Influence of $^{-}NTf_2$ Coordination on $E_{1/2}$ Values

$\Delta E_{1/2} = 0.928$ V





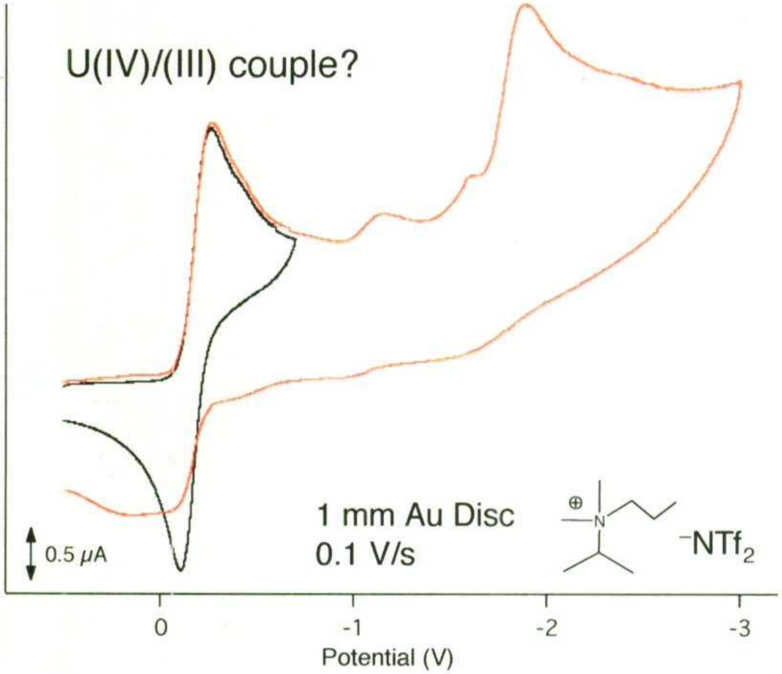
$Cp_2Ti(NTf_2)_2$
$E_{1/2} = -0.103$ V

Cp_2TiCl_2
$E_{1/2} = -1.031$ V

Electrodeposition of Metals from RTIL Solutions

Electrochemical path to "bare" uranium ions

- Uranium metal electrode dissolved directly into RTIL through oxidative electrolysis
- Emerald green solution results indicative of U(IV)
- Coulometry is quantitative for a 4-electron oxidation process
- Voltammetry of resulting solution does not display uranium plating/stripping features



Synthetic path to "bare" uranium ions

$$UCl_4 + 4\,AgNTf_2 \xrightarrow{RTIL} U(NTf_2)_4 + 4\,AgCl$$

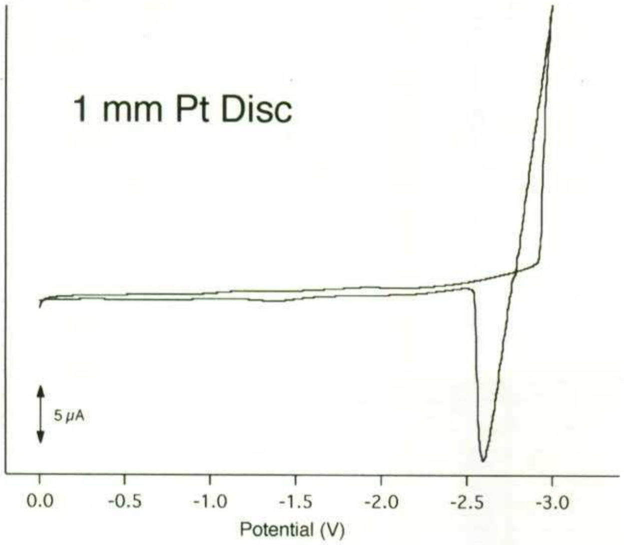
- Green solution results
- AgCl removed through filtration
- Electrochemistry of filtrate does not show U plating; U(IV)/(III) couple may be present

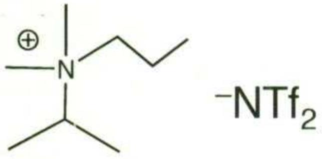
Qualitative electrodeposition data have been obtained for Na, K, Li, and Al using the following metathesis reactions:

$$MH + HNTf_2 \longrightarrow MNTf_2 + H_2$$

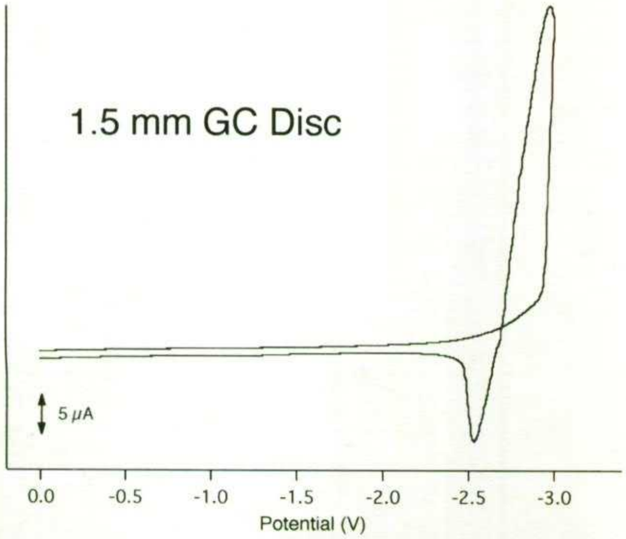
$$Al(CH_3)_3 + 3HNTf_2 \longrightarrow Al(NTf_2)_3 + 3CH_4$$

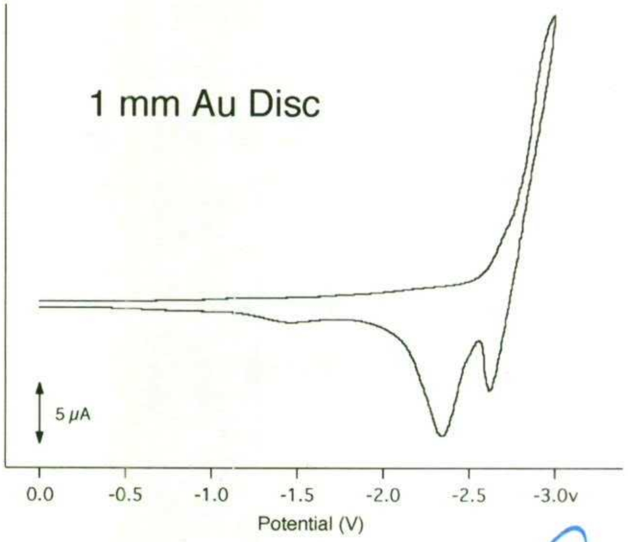
Sodium Electroplating



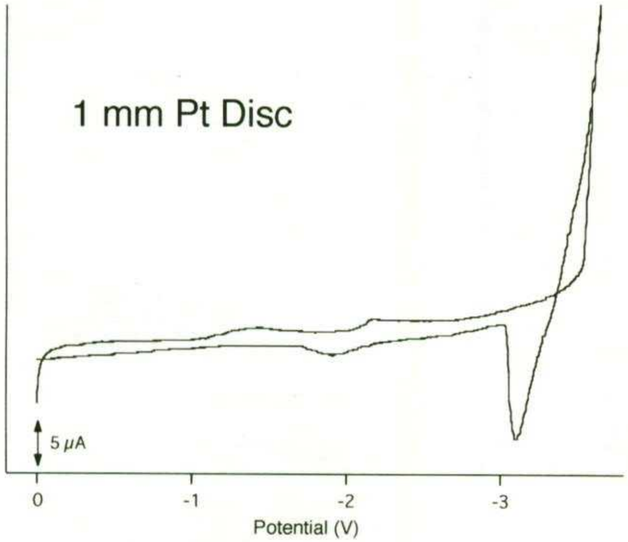


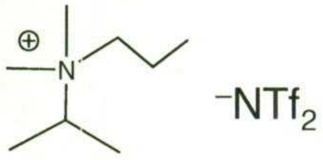
- Conc of "$NaNTf_2$" approx 300 mmol with ca 1.5 times NaH
- 3-electrode cell with Pt aux. and Ag wire ref. in fine glass frits
- For each electrode surface repeatable results obtained



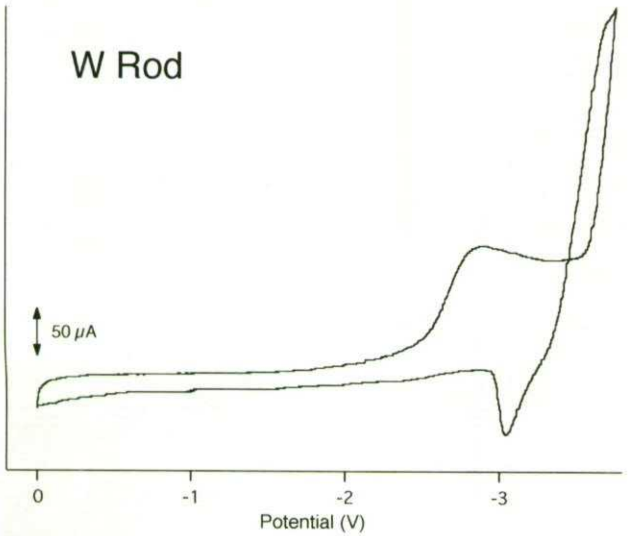


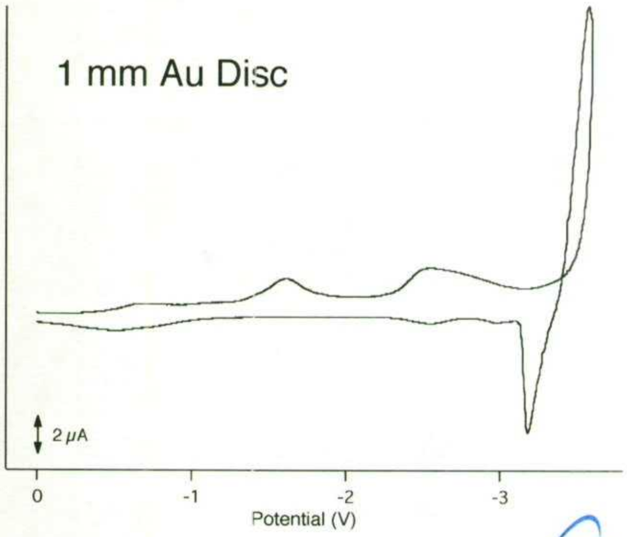
Potassium Electroplating



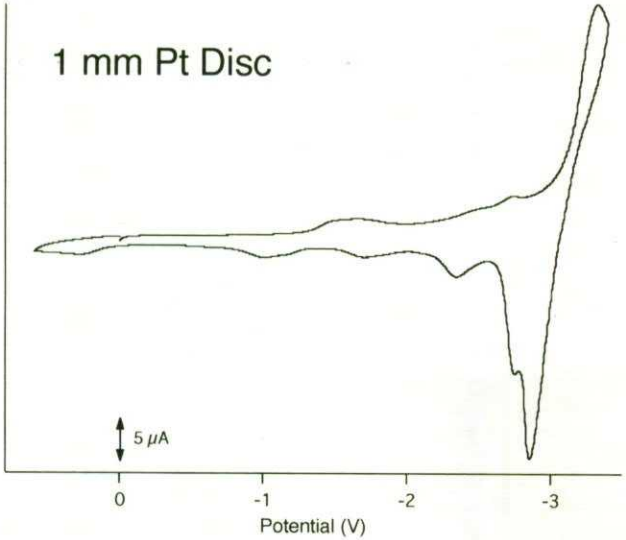


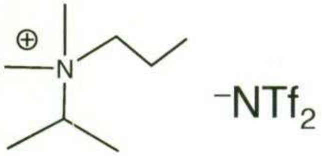
- Electrodeposition not observed on GC electrode



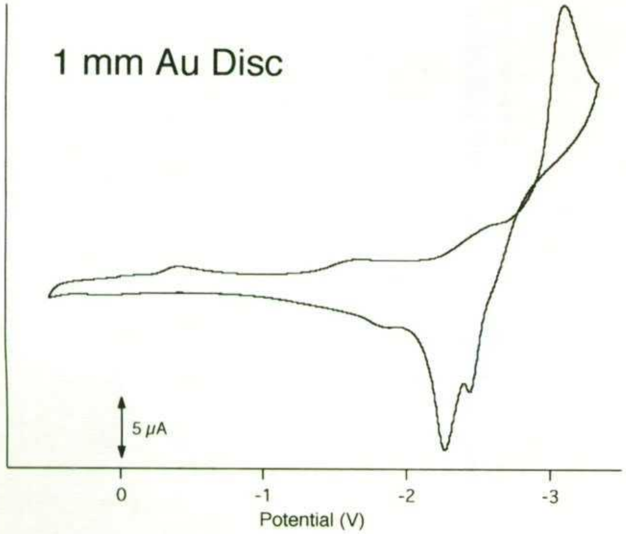


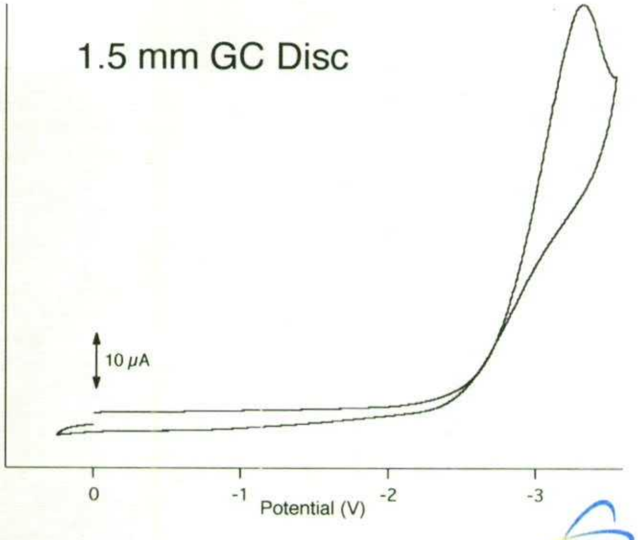
Lithium Electroplating



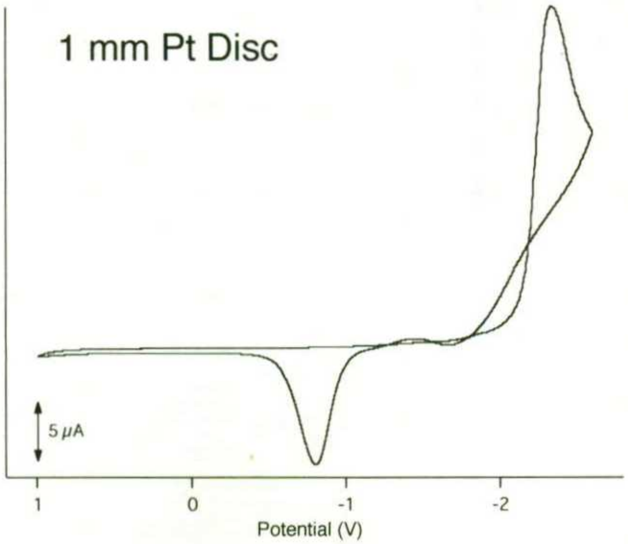


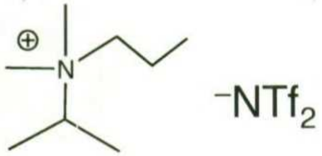
- Conc approx 330 mmol with excess LiH (about 1.5 times)



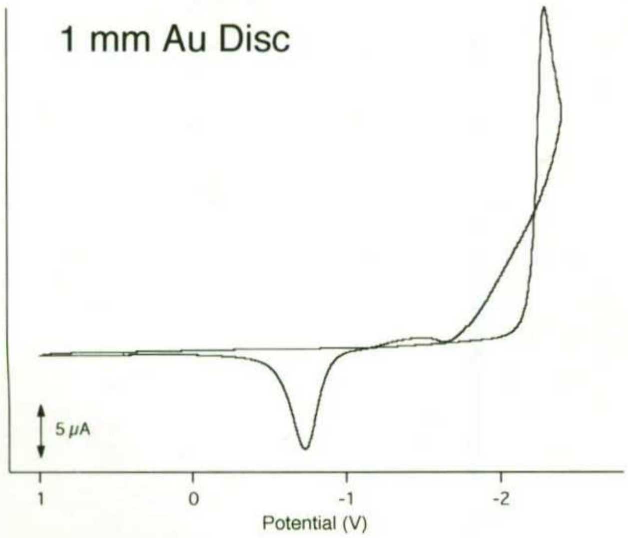


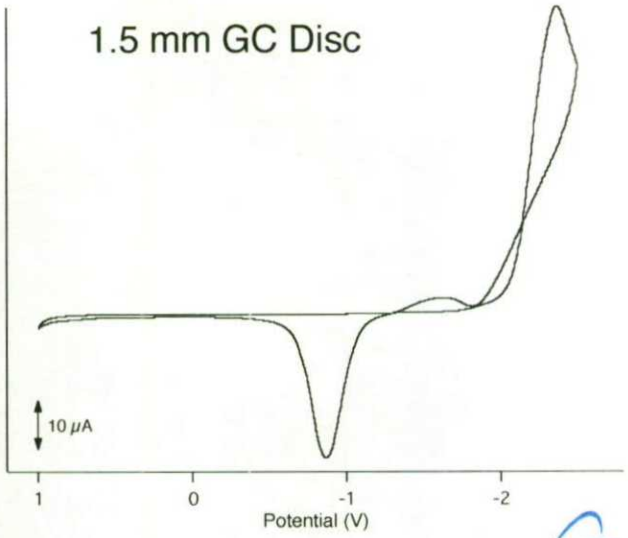
Aluminum Electroplating


1 mm Pt Disc



- Conc. approx. 45 mmol with excess Al_2Me_6


1 mm Au Disc


1.5 mm GC Disc

Summary and Future Directions

- RTIL's are promising solvents for electrochemical applications enabling high-quality data acquisition
  - Exemplified with electrochemical results on several uranium and titanium metal complexes
- Electrochemical plating and stripping demonstrated for mono- and multi-valent electropositive metals

Future Work

- Characterization of $U(V)O_2saldiene^-$ with spectroscopy and x-ray diffraction
- Electroplating:
  - Analysis of metal precipitate on electrode surface with microscopy
  - Quantitative electrochemical analysis
  - Oxidative electrodissolution of metals into RTIL
  - Further studies on the electroplating of actinide metals