An Ultra High Vacuum - Spectroelectrochemical Study of the Dissolution of Copper in the Ionic Liquid (N-methylacetate)-4-picolinium bis(trifluoromethylsulfonyl)imide

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Supporting Information

Ultra high vacuum - spectroelectrochemistry was used to investigate the electrochemically generated copper species in the ionic liquid (N-methylacetate)-4-picolinium bis(trisfluoromethylsulfonyl)imide, [MAP][Tf$_2$N]. The diffusion of Cu$^+$ across the surface of the ionic liquid was monitored *in situ* by X-ray photoelectron spectroscopy (XPS). A numerical procedure was developed to simulate the surface process from which, the apparent diffusion coefficient of Cu$^+$ across the surface is estimated to be $3.5 \times 10^{-5}\,cm^2\,s^{-1}$. Bulk diffusion process of Cu$^+$ in [MAP][Tf$_2$N] was investigated *ex situ* for comparison with the surface process.

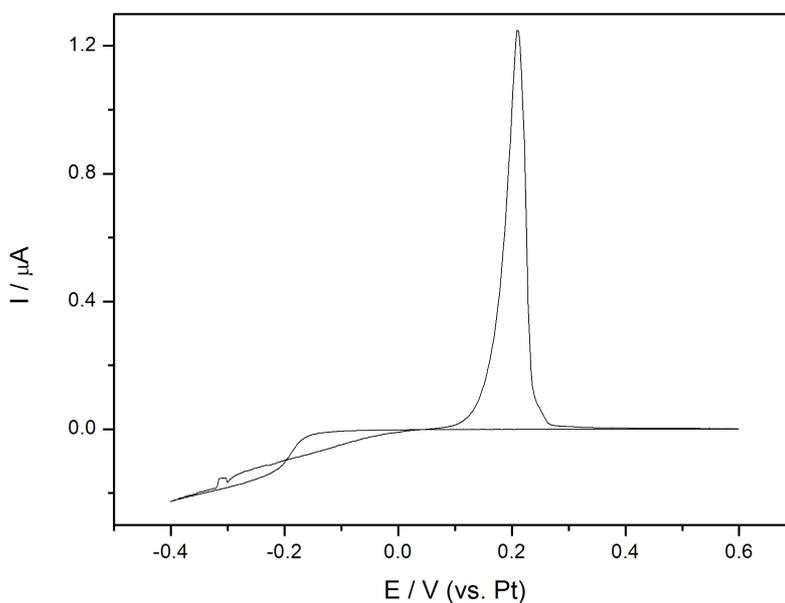*Figure S1. 10 mM Cu(OTf)$_2$ in 0.2 M H$_2$SO$_4$ / H$_2$O at 50 mV s^{-1} using a 25μm Pt microdisc electrode at 298 K.*
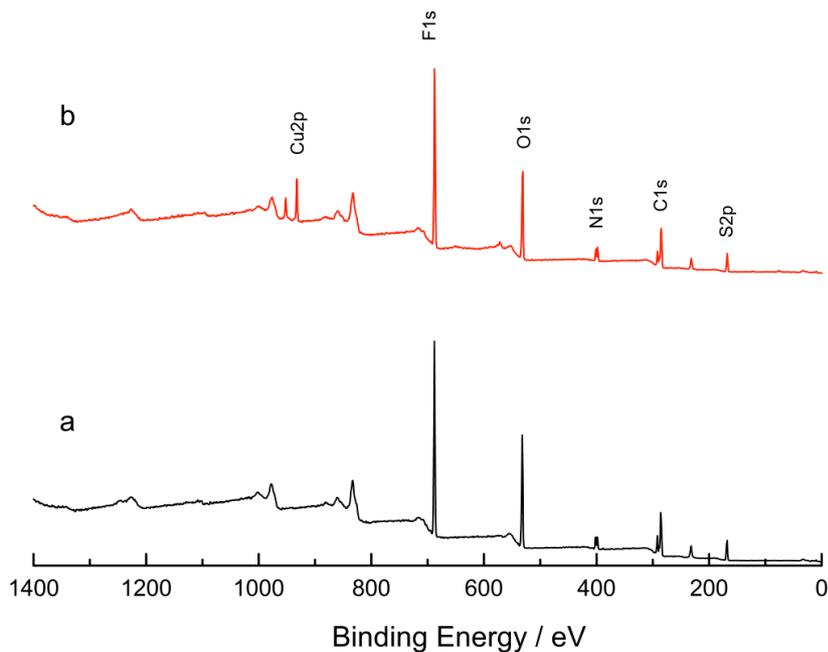
Figure S2. Wide scan XPS spectra before electrolysis (a), and after electrolysis (b) at +1.8 V (vs. Mo stub) in [MAP][Tf₂N].
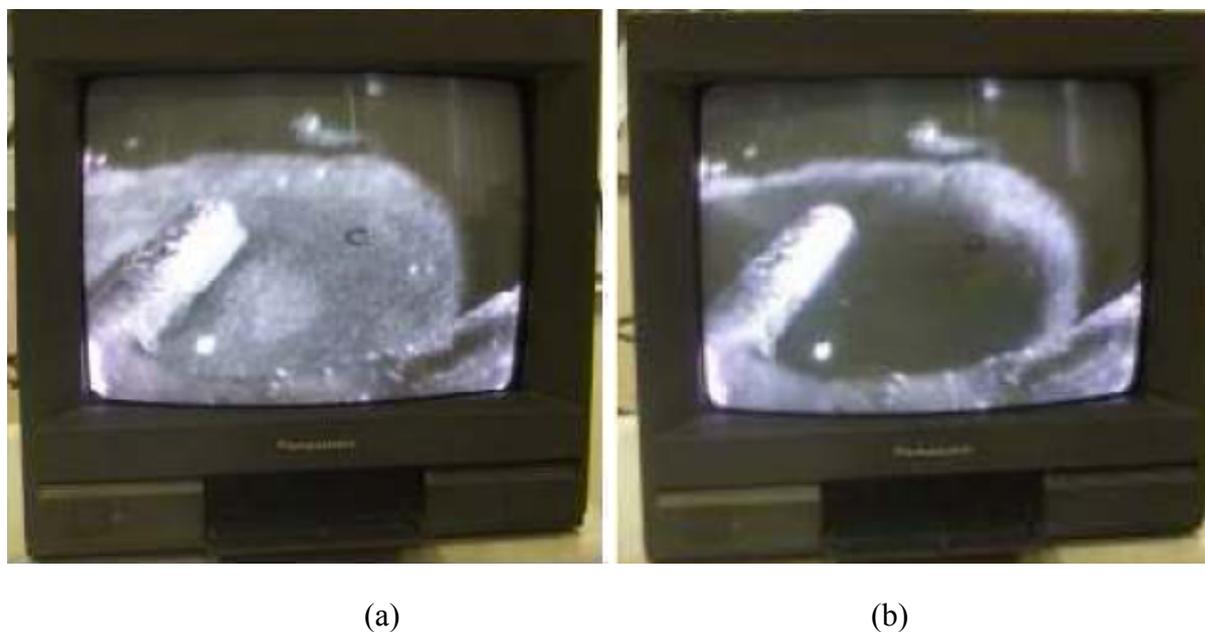

(a)   (b)

Figure S3. Instrument Screen shots illustrating the coloration process of the ionic liquid during the the period of the experiment, (a) image captured before electrolysis and (b) after similar image captured after 90 minutes electrolysis at +1.8 V (vs. Mo stub) in [MAP][Tf₂N]. The back circle is the X-ray irradiation area and the lighter coloured rod is the copper working electrode
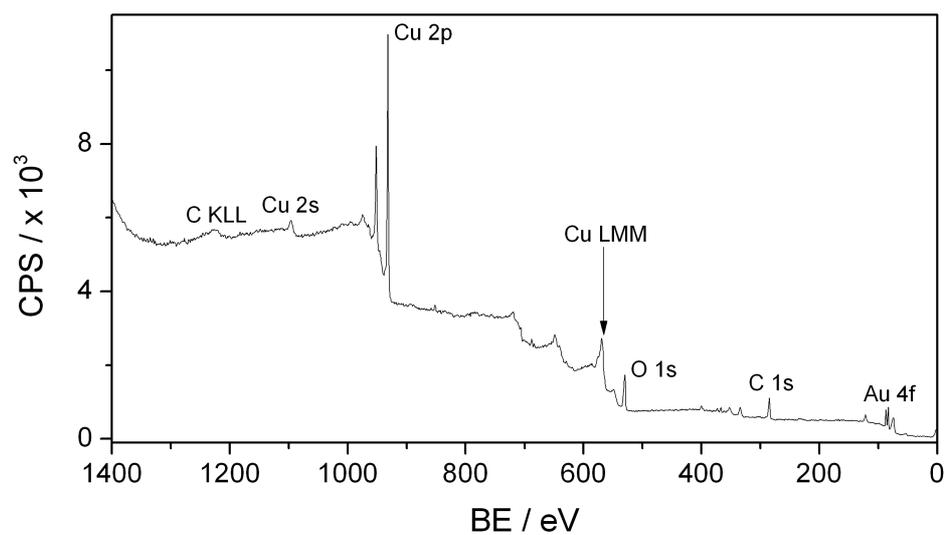
Figure S4. Wide scan XPS spectra of the copper ring deposited on the EC-XPS stub (Au on steel) after electrolysis at +1.8 V (vs. stub) in [MAP][Tf$_2$N].

Temperature / K	Diffusion Coefficient (D) / cm^2 s^{-1}
343	2.43×10^{-8}
353	3.43×10^{-8}
373	6.05×10^{-8}
385	9.32×10^{-8}
398	1.6×10^{-7}

Table SI. Diffusion coefficients (D) calculated using equation (1) for 7.2 mM Cu(TfO)$_2$ in [MAP][Tf$_2$N] at a range of temperatures.

$$I_{\text{lim}} = 4nFDCa \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(1)$$

Where I_{lim} is the steady-state limiting current; n is the number of electron transferred during the electrochemical process; F is the Faraday constant (96485 C mol^{-1}); D *is the* diffusion coefficient of the redox species; C is the bulk concentration of the electroanalyte; and a is the radius of the microelectrode.

		Binding Energy /eV	Conc. / Atom % (Theory)
F 1s		688.8	25.2 (22.2)
O 1s			20.4 (22.2)
-	C=O *(cation)*	534.2	
-	SO$_2$ *(anion)*	532.6	
N 1s			7.6 (7.4)
-	N *(cation)*	402.5	
-	N *(anion)*	399.4	
C 1s			41.5 (40.7)
-	CF$_3$ *(anion)*	292.8	
-	C=O *(cation)*	289.7	
-	C$_{hetero}$ *(cation)*	287.0	
-	C$_{arom}$ *(cation)*	285.9	
S2p		168.9	5.3 (7.4)

Table SII. Binding energies of the major photoelectron peaks and calculated relative atomic percentages for the ionic liquid [MAP][Tf$_2$N]. All binding energies are referenced to F 1s at 688.8 eV.