Supplementary Material (ESI) for Chemical Communications

Spectroelectrochemistry at Ultrahigh Vacuum: *In-situ* Monitoring of Electrochemically Generated Species by X-ray Photoelectron Spectroscopy

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SUPPORTING INFORMATION

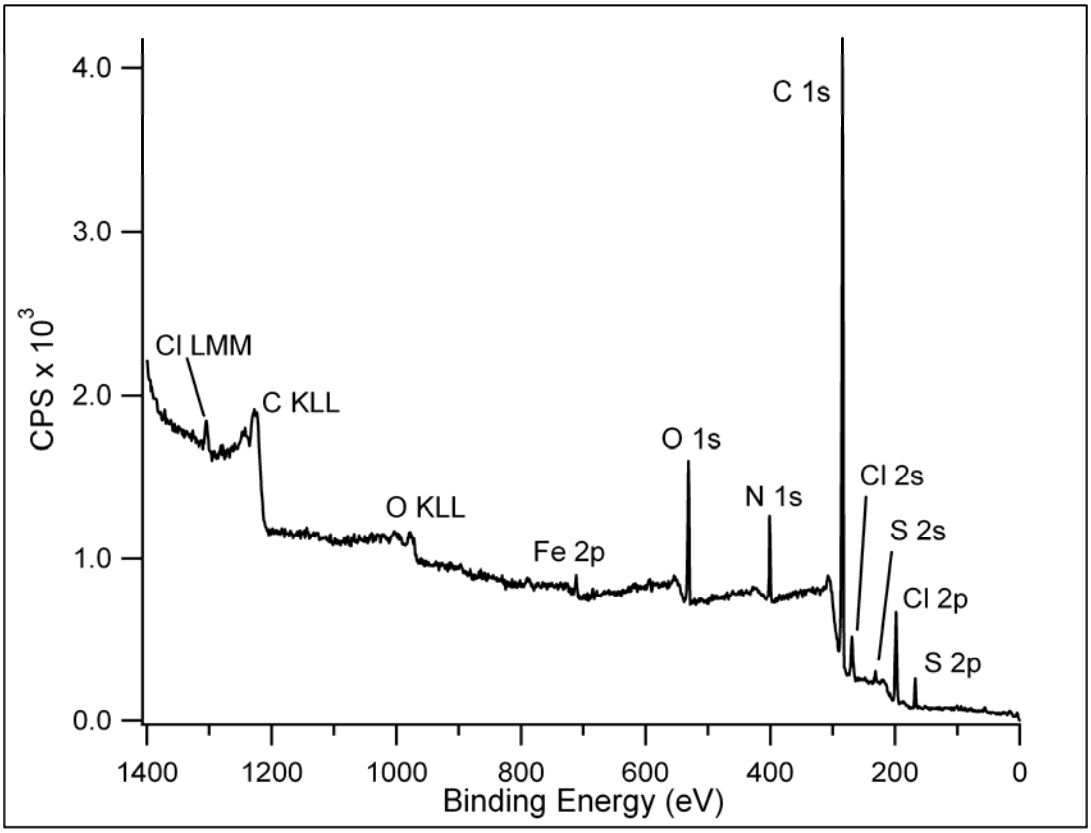
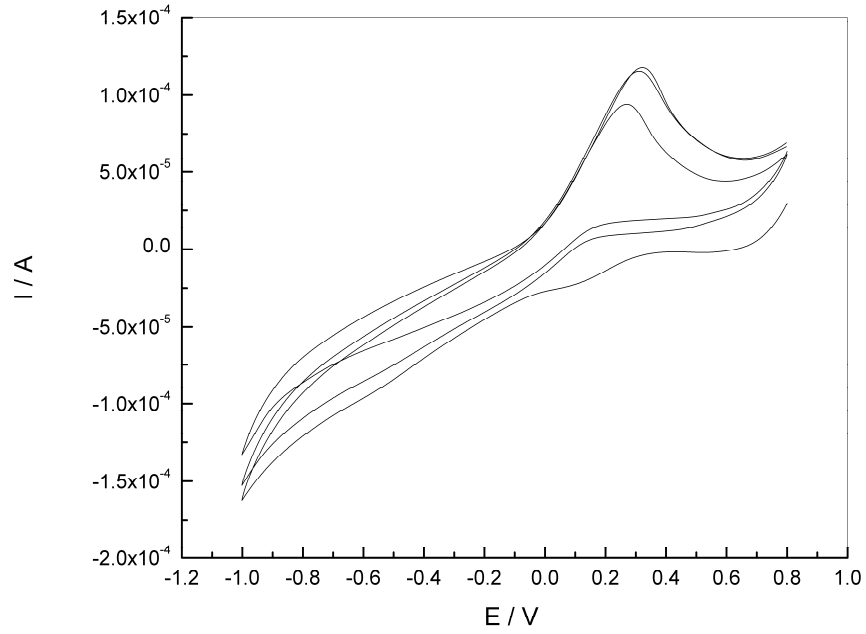
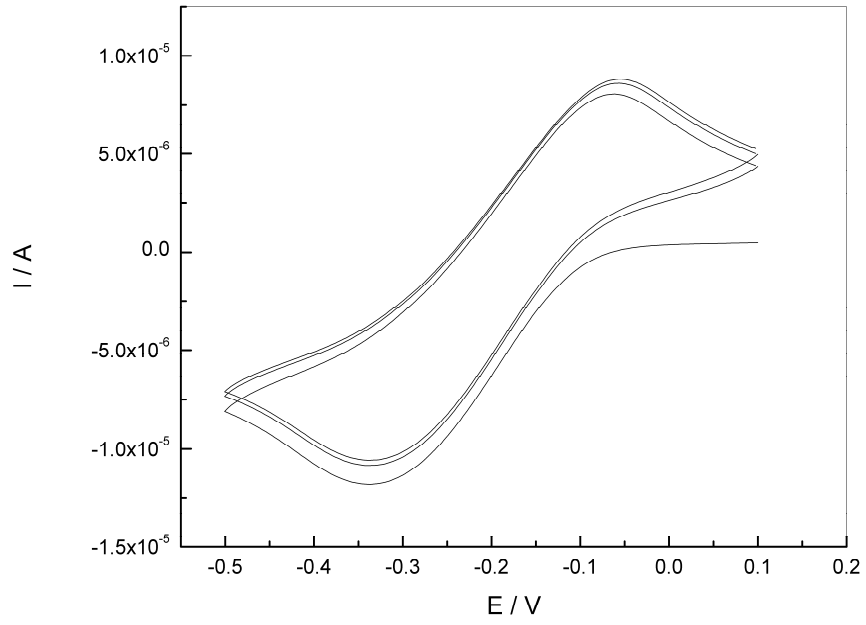


Figure S1 Wide scan spectra of $[C_4MIm][Fe^{III}Cl_4]$ in $[C_2MIm][EtOSO_3]$ (1:2) taken with a pass energy of 80 eV.





(a) (b)

Figure S2 (a) Cyclic voltammogram of $[C_4MIm][Fe^{III}Cl_4]$ in $[C_2MIm][EtOSO_3]$ at 250 mV s^{-1} taken using the 1 mm Pt wire attached to the modified stub (as shown in Figure 1) taken at 1 atm. (b) Cyclic voltammograms of neat $[C_4MIm][Fe^{III}Cl_4]$ taken at a 0.25 mm Pt disc WE using a three electrode set-up with Pt foil counter and reference electrodes.

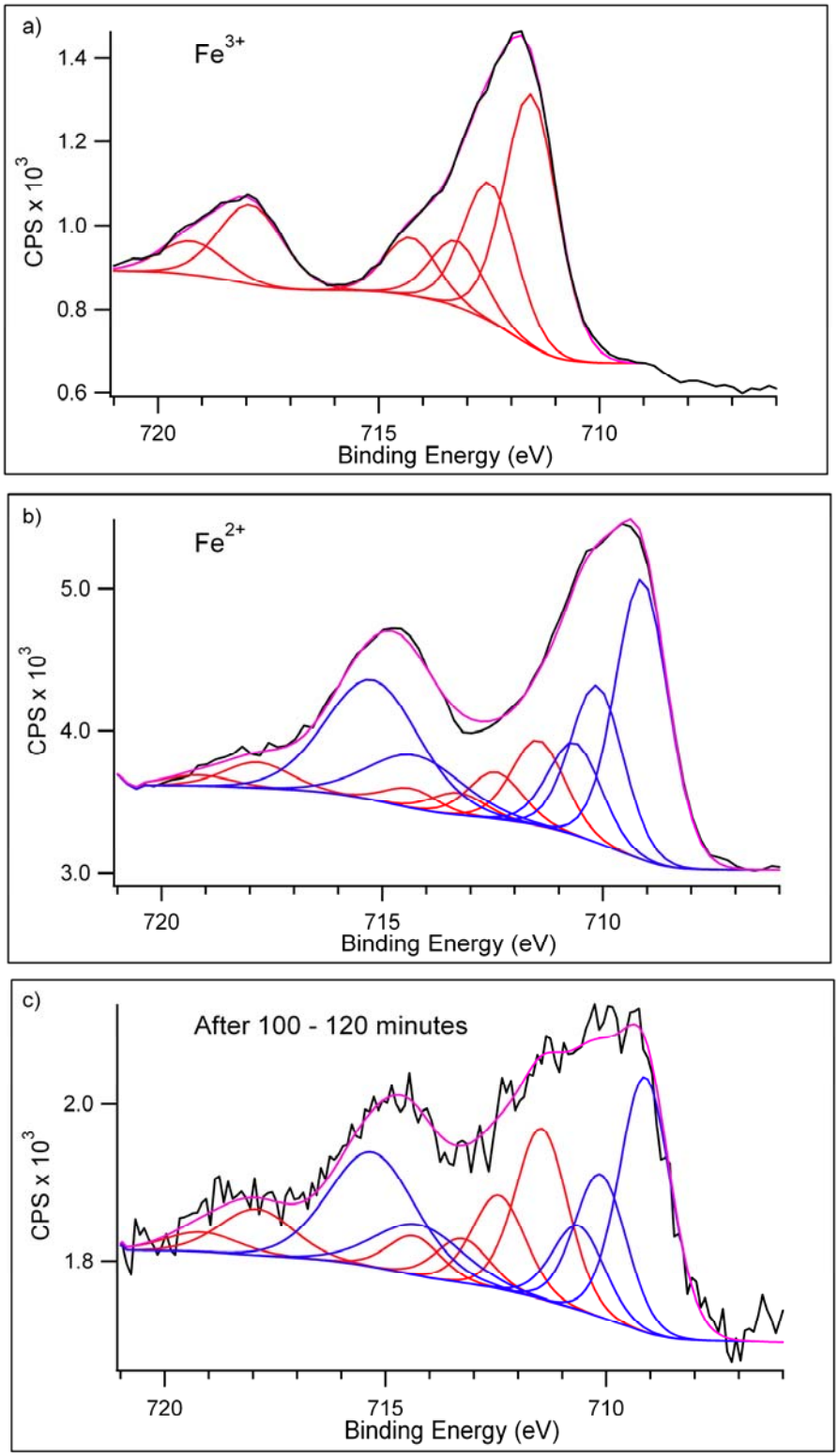


Figure S3 High resolution scans showing fittings of the Fe $2p_{3/2}$ region (pass energy 80 eV) for (a) $[C_4MIm][Fe^{III}Cl_4]$; (b) $[C_4MIm]_2[Fe^{II}Cl_4]$ (showing a small contamination with an Fe^{III} species); (c) $[C_4MIm][Fe^{III}Cl_4]$:$[C_2MIm][EtOSO_3]$ for the scan taken between 100 and 120 minutes of the coulemetric experiment. Components generated using Gupta-Sen fittings[1, 2] as demonstrated by Grosvenor *et al.*[3]

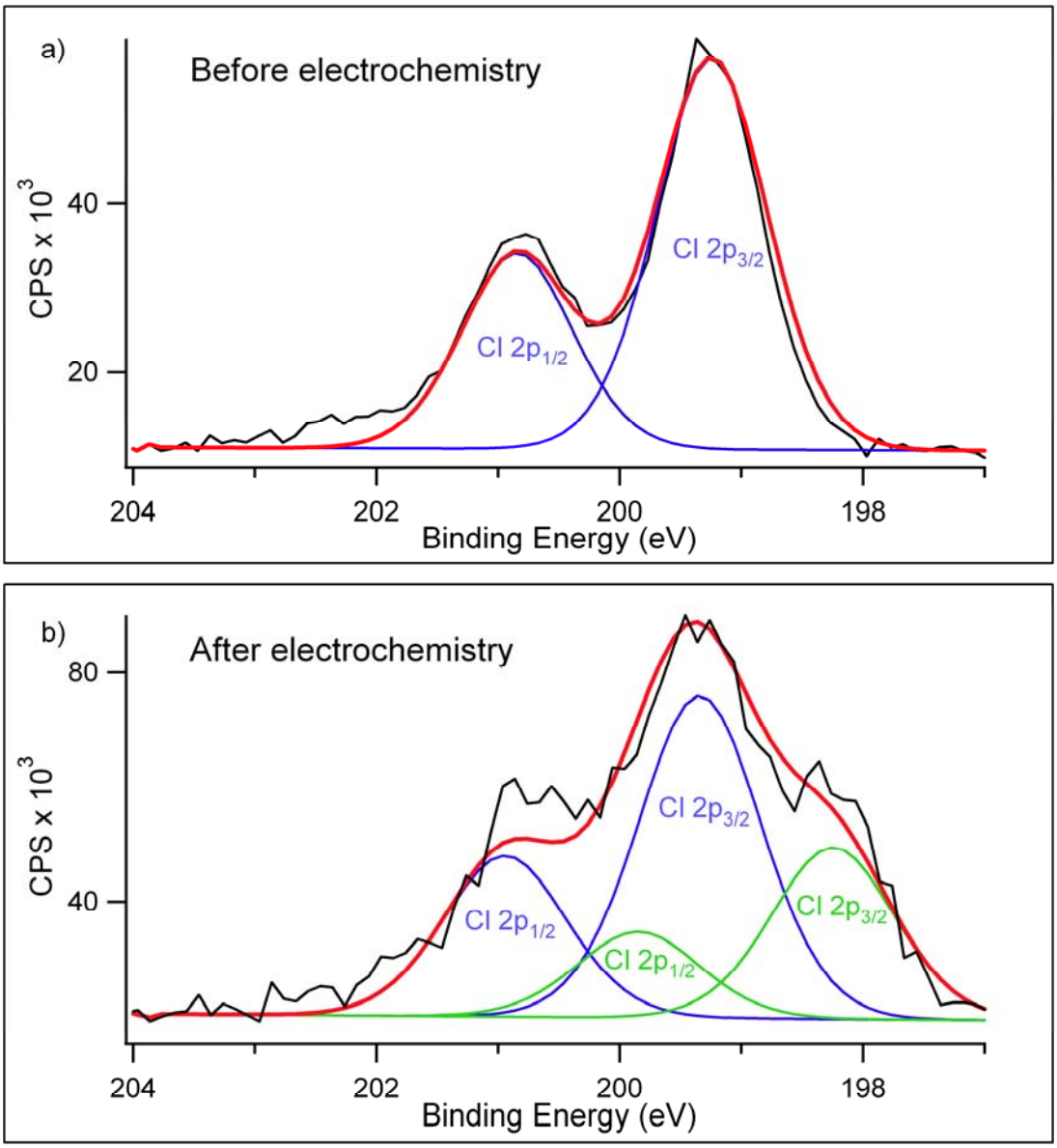


Figure S4 High resolution scans of the Cl 2p regions (pass energy 20 eV) taken (a) immediately before the coulometric experiment began and (b) the following day.

1. R. P. Gupta and S. K. Sen, *Physical Review B*, 1974, **10**, 71-77.
2. R. P. Gupta and S. K. Sen, *Physical Review B*, 1975, **12**, 15.
3. A. P. Grosvenor, B. A. Kobe, M. C. Biesinger and N. S. McIntyre, *Surface and Interface Analysis*, 2004, **36**, 1564-1574.