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Ionometallurgy: Designer Redox Properties for Metal Processing

A.P. Abbott, G. Frisch, S.J. Gurman, A.R. Hillman, J. Hartley, F. Holyoak and K.S. Ryder*

Electronic Supplementary Information

Formulation of liquids

Reline; Choline chloride ($(CH_3)_3NCH_2CH_2OH(Cl)$) (Aldrich 99 %) and urea ($(NH_2)_2CO$) (Aldrich 99 %) were heated and stirred together in a 2:1 molar ratio of choline chloride: urea at *ca.* 75 ^oC until a liquid had formed. The systems were then allowed to cool to *ca.* 25 ^oC before any further analysis was carried out. ***Ethaline*** synthesis was the same as that for Reline but using ethylene glycol ($C_2H_4(OH)_2$) (Aldrich 99 %) in place of the urea.

Electrochemical methods:

Cyclic voltammograms were carried out at the 20 mM concentration of the metal salt (various sources <99 %) using an Autolab PGSTAT 12 potentiostat controlled by GPES software. The three-electrode system consisted of a working electrode, Pt microelectrode (1 mm radius), a platinum counter foil electrode and a silver wire reference electrode. The working electrode was polished with 0.5 µm alumina paste for *ca.* 3 min prior to all measurements, then sonicated to remove any alumina residue and dried. The CV of 20 mM I_2 dissolved in ***Ethaline*** liquid is presented in **Figure 1** below. This clearly shows the two reversible redox peaks in close proximity.

Separation of Zn / Cu mixtures:

Model experiment for metal recovery: A 50 ml solution of 100 mM iodine (1.857 g, 7.32 mmol) in ***Ethaline*** (55.890 g, 50.72 ml) was made up and a mixture of copper powder (0.326 g, 5.13 mmol) and zinc powder (0.323 g, 4.94 mmol) was added. The solution was then left at *ca.* 40 °C and stirred for *c. a.* 24 hours before electrolysis.

EXAFS experimental data:

Extended X-ray absorption fine structure (EXAFS) was recorded on beam line KMC-2 at BESSY II (Berlin). Measurements were carried out on the Cu K-edge (nominally 8979 eV) in total fluorescence yield mode using a double crystal SiGe(111) monochromator and a single element solid state fluorescence detector. The samples were kept in a static flat perspex sample holder (sample thickness 0.5 mm) covered with 40 micron Kapton film. The beam size was 0.1 x 0.7 mm. Samples were aligned at ca. 55° with respect to the beam and the fluorescence detector was positioned perpendicular

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to the beam to minimize the elastic scattering signal. Multiple spectra (4-6) were recorded for each sample and merged with Athena [a]. Background subtraction was performed using PySpline [b]. EXAFS spectra were fitted with EXCURV98 [c] to calculate interatomic distances and their root mean square variation (σ^2). Electron scattering parameters were calculated to determine type and number of coordinating atoms using the Hedin-Lundqvist potential. Quoted uncertainties on fitted parameters are two standard deviations. The EXAFS spectra for 0.1 M $CuCl_2$ in ***Ethaline*** liquid are shown along with best fit data are shown in **Figure 2**.

[a] B. Ravel and M. Newville, J. Synchrotron Rad. 12, 537-541 (2005)

[b] A. Tenderholt, B. Hedman and K.O. Hodgson, SLAC-PUB-12219, (2006).

[c] S. Tomic B.G. Searle, A. Wander, N.M. Harrison, A.J. Dent, J.F.W. Mosselmans and J.E. Inglesfield, CCLRC Technical Report DL-TR-2005-001, ISSN 1362-0207 (2005).

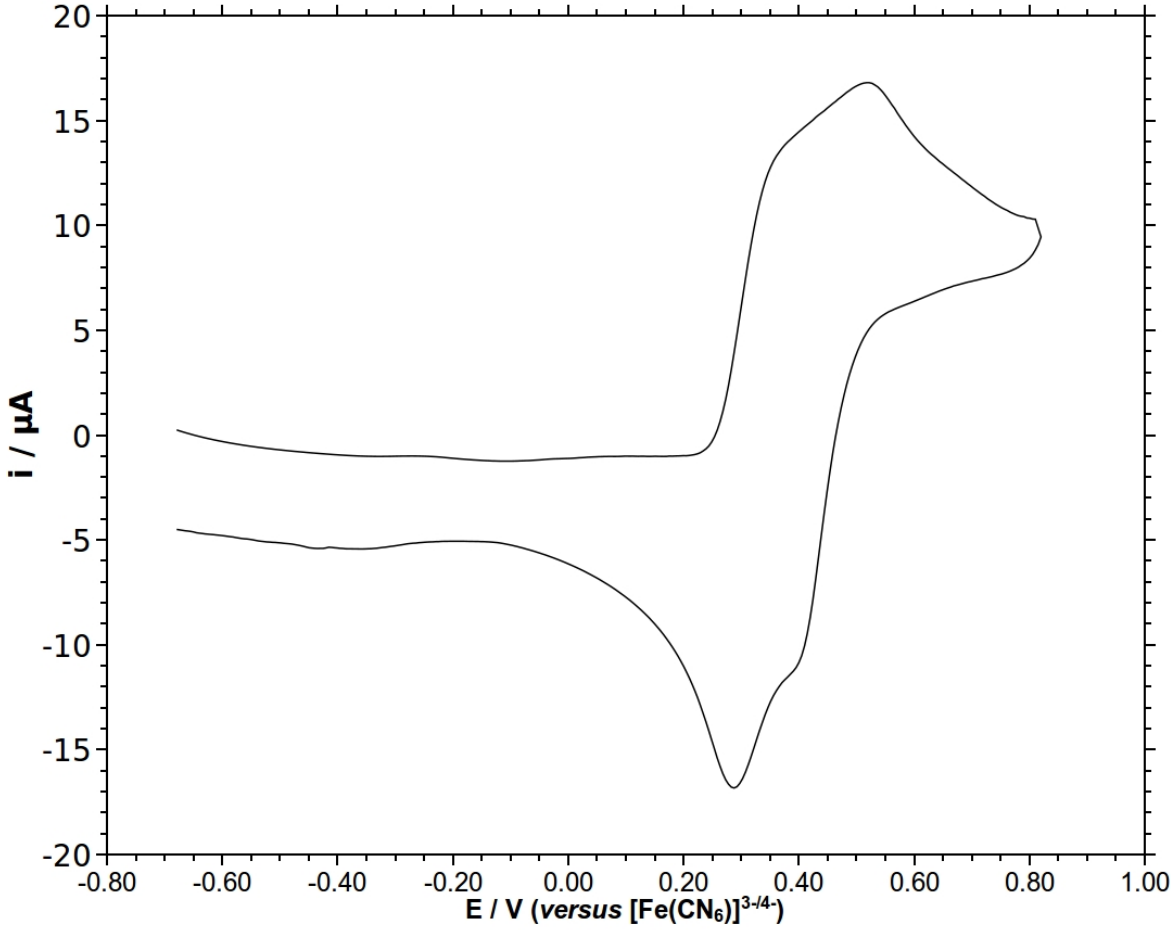
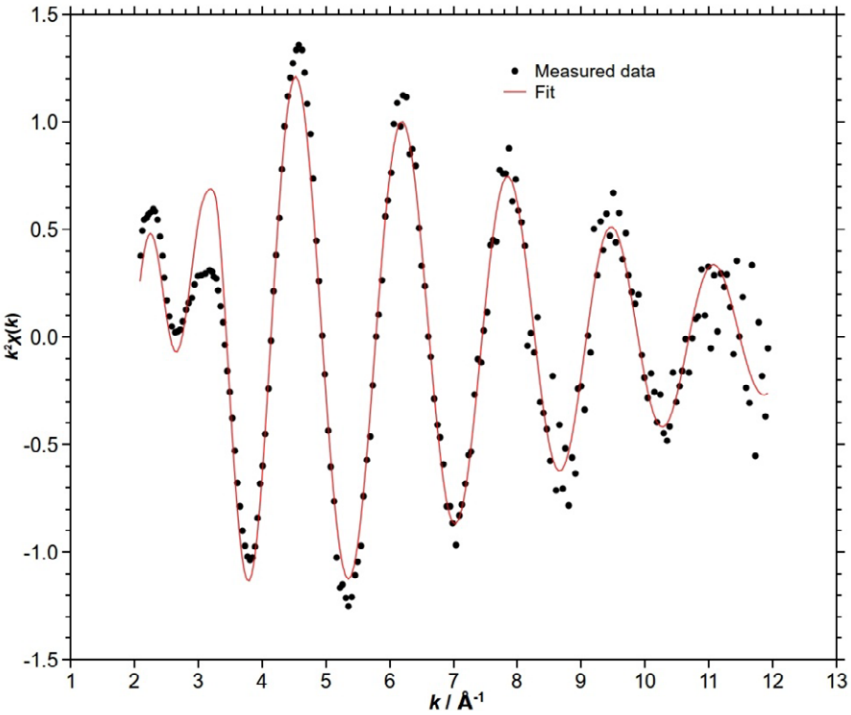
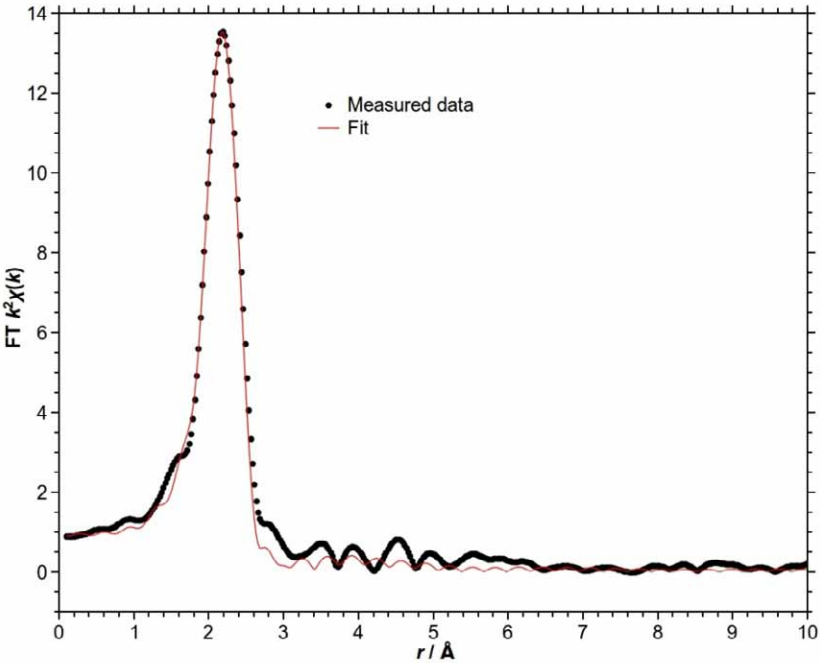


Figure 1 CV of I_2 dissolved in ***Ethaline*** ; concentration of 20 mM at room temp, 1 mm Pt disk working electrode, Ag wire sudo reference electrode at a potential scan rate of 5 mV s-1. The potential scale is referenced against $[Fe\{CN)_6]^{3-/4-}$ as an internal standard.



(a)



(b)

Figure 2 EXAFs data for $CuCl_2$, 0.1 M, in ***Ethaline***; (a) Cu edge data; (b) FT data. The measured data are shown as black circles and the best fit is shown in red. The best fit was obtained gave a stoichiometry of Cu:3.8(2)Cl with a mean Cu-Cl distance of 2.255(4) Å and a residual error, R1, of 4.2 %.