

## Experiment Report Form

**The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.**

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### ***Reports supporting requests for additional beam time***

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### ***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **Deadlines for submission of Experimental Reports**

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

### **Instructions for preparing your Report**

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	<b>Experiment title:</b> Designed speciation for controlled electrodeposition of metal films from novel ionic liquids	<b>Experiment number:</b> CH 3811
<b>Beamline:</b> BM25A	<b>Date of experiment:</b> from: 04.07.2013 to: 08.07.2013	<b>Date of report:</b> 06.01.2014
<b>Shifts:</b> 12	<b>Local contact(s):</b> Alvaro Munoz-Noval	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): G. Frisch* (Institut für Anorganische Chemie, TU Bergakademie Freiberg) J. Hartley* (Institut für Anorganische Chemie, TU Bergakademie Freiberg) A. Azeez* (University of Leicester, Department of Chemistry) A. Abbott (University of Leicester, Department of Chemistry) K. Ryder (University of Leicester, Department of Chemistry) S. J. Gurman (University of Leicester, Department of Physics)		

### Report:

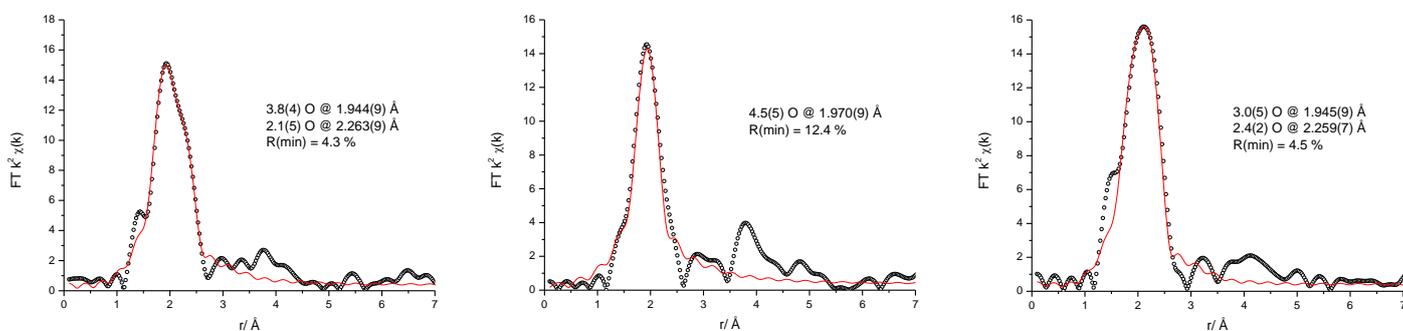
EXAFS spectra were acquired for chromium, cobalt and zinc salts in the form of eutectic mixtures created with either choline chloride, or hydrogen bond donors, such as urea, 1,2-propylene glycol or ethylene glycol. Samples were measured at room temperature, except for selected chromium samples which were measured at elevated temperatures. The effect of the addition of up to 20 % water to the chromium samples was also investigated. Solid salt samples were obtained for reference purposes.

Data quality was mostly good with spectra being usable to at least 12 Å<sup>-1</sup>. The cobalt and zinc spectra were generally glitch free, however several major glitches were observed in the chromium spectra, both before and after the edge (5830, 5920, 5970, 6371, 6459 and 6490 eV). Samples were measured in thin films between perspex sheets in transmission mode, with the solid samples being diluted in a cellulose matrix. The thickness of the liquid samples was between 20 and 200 microns. Part of this experiment was to record the EXAFS spectra of samples at elevated temperatures, however in most cases fluctuations in temperature of only < 5 °C already produced such large fluctuations in sample thickness that the data could not be analysed with standard techniques. We are currently trying to modify our methods of background subtraction accordingly.

Metal-ligand distances were calculated to be ca. 1.9 Å for M-O and 2.2 to 2.5 Å for M-Cl, which is consistent with both the solid reference samples and previous experimental data.

In most cases, the Fourier transforms of the chromium data could be fitted with a double peak, which suggested that the speciation was composed of mixed chloro-oxo species, the ratio of which depended on the additional component of the system. The only solution to show a single peak was the 4:1 urea:Cr system. Solutions containing no more than 67% urea tended toward the formation of the cationic species, e.g.  $[\text{CrCl}_2(\text{OD})_4]^+$ , where the oxygen donor was either water or urea. This speciation is maintained, even with the addition of significant amounts of water (up to ca. 20% by mass). The presence of urea in the coordination was identified by a broad peak in the FT at ca. 4 Å, which was more pronounced in the high urea content samples. As this peak was not able to be included in the data fits, the exact urea:water ratio remains unknown.

Solutions based on choline chloride showed chromium was coordinated by a higher proportion of chloride ions, suggesting that a mixture of both anionic and cationic species are present. This is in agreement with UV-Vis data of these systems, which suggest that the ChCl-based system contains a greater proportion of chloride in the coordination shell of the chromium atom than the urea-based system.



*Fourier transforms of the EXAFS data (black circles) and fits (red line) for 1:2(l) and 4:1 (m) urea:CrCl<sub>3</sub>·6H<sub>2</sub>O and 1:2 ChCl:CrCl<sub>3</sub>·6H<sub>2</sub>O.*

The EXAFS spectra for zinc and cobalt suggest that more complex species are being formed in the solutions with a higher metal content (greater than 50 % metal salt). This is evidenced by the appearance of peaks between 3 and 5 Å in the Fourier transform, which we were not able to fit yet. Possible identities for these peaks are coordination with nitrate or glycol, or even formation of polynuclear species.

In samples with lower metal percentages (25 % metal salt), the speciation is strongly affected by the ligand already present on the metal salt, with the chloride salts forming tetrachloro species.

These results have allowed us to understand how the molar fraction of metal salt affects the speciation of the metals in Type 1, 2 and 4 eutectic mixtures. These changes coincide with changes in the electrochemical properties, i.e. deposition morphology and passivation effects. Mechanistic studies for the Co and Zn systems are subject of ongoing research.

The results for chromium have been submitted for publication to Phys. Chem. Chem. Phys.