



	Experiment title: Speciation of copper complexes in binary mixtures of ionic liquids and water	Experiment number: 26-01 870
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Report:

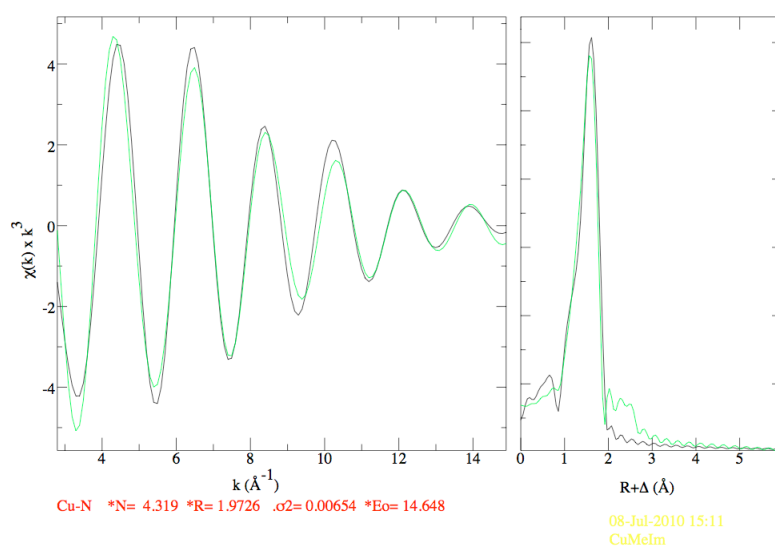
The redox chemistry of copper in ionic liquids differs from that in aqueous solution, because in an ionic liquid copper(I) and not copper(II) is the most stable species. One of the aims of this proposal was to investigate by XAS the speciation of copper in binary mixtures of chloride and bromide ionic liquids with water, in order to investigate how the redox and coordination chemistry of copper(II) gradually changes from an ionic liquid to a water regime upon addition of increasing amounts of water to the ionic liquid.

Because of their high electric conductivity and wide electrochemical window, ionic liquids are very suitable electrolytes that can be used for the electrodeposition of reactive metals that cannot be deposited from aqueous solution. Even for metals that can be electrodeposited from water, ionic liquids offer nevertheless interesting possibilities because the morphology of a metal layer obtained in an ionic liquid is often different from one deposited from an aqueous solution. Moreover, it is possible to obtain from an ionic liquid alloys with compositions different from that formed in aqueous solution. The redox chemistry of metals that have ions with different oxidation states strongly depends on the environment. For instance, in the case of *copper*, copper(II) is the most stable species in aqueous solution whereas in ionic liquids, copper(I) is the most stable form. This means that for electrodeposition of copper, the redox couple Cu^+/Cu is operative in ionic liquids, whereas for aqueous solutions the ruling redox couple is Cu^{2+}/Cu . As a consequence, when a copper(II) salt is dissolved in an ionic liquid and when this copper(II) solution is brought into contact with copper metal, a comproportionation reaction occurs: $\text{Cu}^{2+} + \text{Cu} \rightarrow 2 \text{Cu}^+$. The standard redox potentials strongly depend on the type of copper complexes that are present in solution. For instance, $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ can easily be reduced to Cu, whereas the reduction of $[\text{CuCl}_4]^{2-}$ is much more difficult.

It is difficult to work with ionic liquids in strictly anhydrous conditions with rigorous exclusion of water.

This can only be achieved in a state-of-the-art glovebox or with Schlenk line techniques. This working in anhydrous conditions is also from a technological point of view not interesting and the electrodeposition of copper from an ionic liquid electrolyte exposed to the atmosphere is preferred from electrodeposition in a glove box. The question arises how much water can be tolerated in the ionic liquid so that the electrodeposition still remains “ionic liquid like”. Therefore, one series of samples was studied during this experiment, in order to investigate the influence of the water content in the ionic liquid on the coordination sphere of the copper ion. The analysis of this sample series is still ongoing, but it is nevertheless clear that interesting changes occur in this series upon changing the water content.

A second aim of this project was to study a series of new metal containing ionic liquids that have the metal as part of the cation in view to using these liquids as electrolytes for electrodeposition of metals. The synthesis of these ionic liquids has already been published. [1] In this project, XAS was used to probe the first coordination sphere of the copper(I) ion and to compare this with crystal structures that had been obtained from single crystals grown from the frozen liquids earlier. In a typical example, the EXAFS spectrum was recorded from a copper(I)-containing ionic liquid, in which the copper(I)-ion is coordinated by nitrogen atoms (for example in a methyl imidazolium ligand). Because of the complexity of the organic structure of the ligand, it can be quite tedious to fit the spectrum with a high degree of accuracy (multiple scattering effects can be hard to incorporate fully in order to get a satisfactory result), and therefore, the peak in the spectrum, corresponding to the first shell of nitrogen atoms was filtered out, back Fourier transformed and then fitted, using a model derived from the crystal structure. In the figure below, such a fit is shown.



In this specific example, a coordination number close to 4 is found, which is in agreement with a typical tetrahedral coordination mode, often encountered for copper(I). Even with these preliminary results, however, it became clear that simply comparing coordination spheres from the room temperature or frozen structures would not give us the necessary information about the (higher temperature) molten state that we were interested in. That is why a follow-up experiment would be quite interesting, in which the temperature of the sample could be varied during the measurement. That is the subject of our new proposal, which has been given the reference number 26-01 906.

Reference:

- [1] S. Schaltin, N. R. Brooks, K. Binnemans and J. Fransaer, *J. Electrochem. Soc.*, (2010) paper accepted for publication