# Supporting information

## Towards an all-copper redox flow battery based on a copper-containing ionic liquid

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## Experimental

Tetrakis(acetonitrile) copper(I) bis(trifluoromethylsulfonyl)imide (abbreviated as $[Cu(MeCN)_4][Tf_2N]$) was prepared according to a literature procedure, by reacting copper(II) oxide with bis(trifluoromethylsulfonyl)imidic acid in water to yield copper(II) bis(trifluoromethylsulfonyl)-imide [1]. The copper(II) salt $Cu(Tf_2N)_2{\cdot}4H_2O$ was isolated by drying *in vacuo* and then redissolved in acetonitrile. A comproportionation reaction between copper metal (added as a powder) and the copper(II) ions yielded $[Cu(MeCN)_4][Tf_2N]$, which was then isolated by removing the solvent acetonitrile *in vacuo*. The reaction sequence is:

$$CuO + 2\ H[Tf_2N]_{aq} \rightarrow Cu(Tf_2N)_2 + H_2O \quad (1)$$

$$Cu(Tf_2N)_2 + Cu + 8\ MeCN \rightarrow 2\ [Cu(MeCN)_4][Tf_2N] \quad (2)$$

The melting point of $[Cu(MeCN)_4][Tf_2N]$ is 66 °C and the concentration of copper in this compound is 3.1 mol $dm^{-3}$. More details on the synthesis and chemical characterization of $[Cu(MeCN)_4][Tf_2N]$ can be found elsewhere [1].

Voltammetry and RDE experiments were performed in an argon-filled glove box. The experiments were done using a Potentiostat/Galvanostat EG&G 273 controlled by a computer with Corrware software. All potentials are relative to a copper wire directly immersed in solution (pseudo-reference electrode). The electrode was a platinum disk (diameter of 3 mm). The rotation rate of the rotating disk electrode was controlled by a Metrohm Autolab RDE controller. All electrochemical experiments were performed at 90 °C.

Charge-discharge experiments were executed in a commercially available closed H-type glass cell consisting of two double-walled compartments (1 mL each, corresponding to a charge of 300 C). It was purchased from SES GmbH - Analytical Systems. The temperature was set by pumping water, whose temperature was controlled by a standard laboratory heating pump, through the outer wall.

The compartments are separated by a Morgane$^{TM}$ membrane, which is a cross-linked post-quaternized ethylene tetrafluoroethylene-chloromethylstyrene copolymer (anion exchange membrane [2]). Each compartment was mixed by a small magnetic stirrer. The anode and cathode were two platinum spiral electrodes. A current of 2 mA was applied during both charging and discharging of the cell, and the discharge cut-off voltage was 0.0 V.

## References

[1] N. R. Brooks, S. Schaltin, K. Van Hecke, L. Van Meervelt, K. Binnemans, J. Fransaer, Copper(I)-containing ionic liquids for high-rate electrodeposition, Chem. Eur. J. 17 (2011) 5054.

[2] T. Xu, Ion exchange membranes: state of their development and perspective, J. Membrane Sci. 263 (2005) 1.