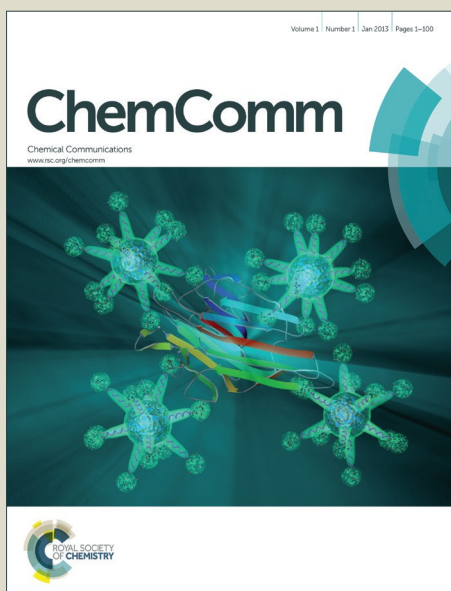


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Towards an all-copper redox flow battery based on a copper-containing ionic liquid[†]

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The first redox flow battery (RFB), based on the all-copper liquid metal salt [Cu(MeCN)₄][Tf₂N], is presented. Liquid metal salts (LMS) are a new type of ionic liquid that functions both as solvent and electrolyte. Non-aqueous electrolytes have advantages over water-based solutions, such as a larger electrochemical window and large thermal stability. The proof-of-concept is given that LMSs can be used as the electrolyte in RFBs. The main advantage of [Cu(MeCN)₄][Tf₂N] is the high copper concentration, and thus high charge and energy densities of 300 kC l⁻¹ and 75 W h l⁻¹ respectively, since the copper(I) ions form an integral part of the electrolyte. A Coulombic efficiency up to 85% could be reached.

The need for clean, renewable energy sources is causing a shift from fossil fuel to wind and solar energy. These two types of sustainable energy sources are widely available and the most practical to implement. However, their intermittent nature requires ways to balance the difference between the instantaneous supply and demand of electric energy since it is currently not possible to store large amounts of electricity. An obvious solution is to store electricity under the form of chemical energy, i.e. in batteries. Only redox flow batteries have a storage capacity that is compatible with the production capacity of a large wind turbine or a solar cell farm. *Redox flow batteries* (RFBs) are therefore heavily studied to balance the production and consumption of electrical energy^{1,2}. RFBs store chemical energy in the form of dissolved

redox couples in external tanks. Electricity is generated in a separate power module. During discharge, the two electrolytes flow from the separate storage tanks to the electrolysis cell for the redox reaction, with ions transferred between the two electrolytes across an ion-exchange membrane. A comprehensive review on ion-exchange membranes was written by Xu³. After the reaction, the spent electrolytes are returned to the storage tanks. During the recharging step, the process is reversed.

Although aqueous RFBs are well studied and commercially available, RFBs based on non-aqueous electrolytes are starting to gain interest. The main reasons are the small electrochemical window of water and the low concentration of electroactive species, which limit the energy content that can be stored in aqueous RFBs. By switching from water to organic solvents the potential differences between the redox couples involved can be increased, because the redox couples that can be used are not restricted by the electrochemical window of water (i.e. 1.23 V). Such larger potential differences between the two redox couples can increase the energy density of the redox flow battery. Examples of nonaqueous RFB systems can be found in the literature^{4–11}. Unfortunately, organic solvents are often volatile, have safety issues and metal salts are often only sparingly soluble in them.

Ionic liquid RFBs benefit from larger electrochemical windows, low volatility, intrinsic electrical conductivity and a good thermal stability. Ionic liquids have also been used as supporting electrolytes in organic solvents¹². On the other hand, studies of redox couples for RFBs in ionic liquids are scarce^{13,14}, although they can be a promising electrolyte medium^{15,16}. Even more promising solvents are metal-containing ionic liquids, also known as *liquid metal salts* (LMS)^{17–22} or *MetILs*^{23–26}.

As a proof-of-concept, an all-copper RFB is described here with the copper(I)-containing LMS [Cu(MeCN)₄][Tf₂N] as the electrolyte (MeCN = acetonitrile, figure 1). This LMS has been used previously as electrolyte for the high-rate electrodeposition of metallic copper layers^{17,18}. Two types of all-copper RFBs have

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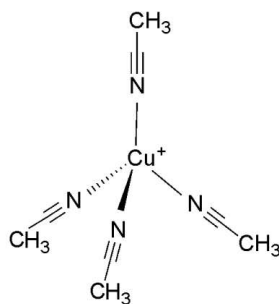
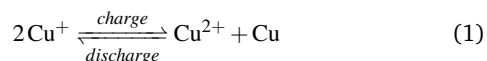


Fig. 1 Structure of the $[\text{Cu}(\text{MeCN})_4]^+$ cation

been reported recently, one in aqueous and another one non-aqueous media^{27,28}, but not yet in the application of LMS. In this paper, it is shown that LMS are promising electrolytes for RFBs. When a redox-active metal ion is part of the anion, cation or both, very high metal ion concentrations can be achieved and, hence, a large charge and energy density. In the case of $[\text{Cu}(\text{MeCN})_4][\text{Tf}_2\text{N}]$, the charge density is 300 kC l^{-1} , so for a theoretical voltage of 0.9 V (*vide infra*) this corresponds to an energy density of 75 W h l^{-1} which is several factors higher than the value of commercially available RFBs.

Cyclic voltammograms of $[\text{Cu}(\text{MeCN})_4][\text{Tf}_2\text{N}]$ were measured at 90°C (figure 2). This temperature was chosen because of the melting point of $[\text{Cu}(\text{MeCN})_4][\text{Tf}_2\text{N}]$ (66°C) and was a compromise between decreasing the viscosity and keeping the liquid metal salt stable since at higher temperatures, acetonitrile ligands evaporate.¹⁷ At 90°C some MeCN ligands will evaporate but, since the cell is closed, this would lead to a quick build-up of pressure, stopping further evaporation. Different scan rates were applied in the potential interval from -0.3 V to $+1.75 \text{ V}$. In $[\text{Cu}(\text{MeCN})_4][\text{Tf}_2\text{N}]$, two redox couples can be observed: not just the Cu^{2+}/Cu , as in aqueous solutions, but also $\text{Cu}^{2+}/\text{Cu}^+$ and Cu^+/Cu are accessible in $[\text{Cu}(\text{MeCN})_4][\text{Tf}_2\text{N}]$. This LMS has the additional advantage that it is electrochemically stable over the entire applied potential range. The only species that can react electrochemically is the $[\text{Cu}(\text{MeCN})_4]^+$ -moiety. If MeCN or the anion $[\text{Tf}_2\text{N}]^-$ would react as well, this would be visible as parasitic reactions during the voltammograms, which is not the case. The presence of two redox couples for copper is often observed in ionic liquids and LMS^{17,18,29–32}. The couple Cu^+/Cu is situated at 0.0 V and $\text{Cu}^{2+}/\text{Cu}^+$ around $+0.9 \text{ V}$. This means that a battery with $[\text{Cu}(\text{MeCN})_4][\text{Tf}_2\text{N}]$ as electrolyte could theoretically provide a voltage of 0.9 V with following charge/discharge reactions:



In this equation, the Cu^{2+} species is most likely present as a $[\text{Cu}(\text{MeCN})_4]^{2+}$ -moiety seeing as there are no extra ligands to bind to the $\text{Cu}(\text{II})$ ion and that four-fold coordination for $\text{Cu}(\text{II})$ is very common. Hence, the principle of this battery hinges on the fact that in this liquid metal salt, Cu^+ is the thermodynamically stable valence state, as opposed to water where Cu^{2+} is the stable valence state. The influence of the scan rate is mostly noticeable for the $\text{Cu}^{2+}/\text{Cu}^+$ couple. This can be explained by the fact that

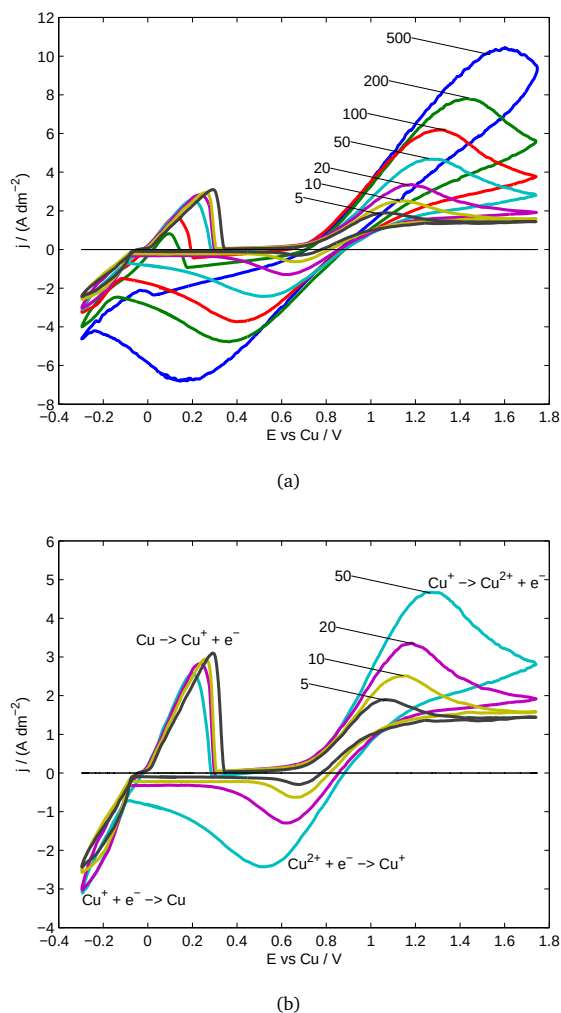


Fig. 2 Cyclic voltammograms of $[\text{Cu}(\text{MeCN})_4][\text{Tf}_2\text{N}]$ at 90°C . The labels indicate the scan rate (in mV s^{-1}). Figure (b) is similar to figure (a) but the voltammograms with scan rates of 100, 200 and 500 mV s^{-1} have been omitted for clarity.

the reduction for the couple Cu^+/Cu is not limited by mass transport¹⁷. The oxidative stripping wave is solely determined by the amount of deposited copper on the electrode and is thus also not mass-transport-limited. From figure 2, it is clear that both redox couples $\text{Cu}^{2+}/\text{Cu}^+$ and Cu^+/Cu are active in the reduction direction as well as the oxidation direction. For the $\text{Cu}^{2+}/\text{Cu}^+$ redox couple however, there is a change in peak potential with varying scan rates, indicating the process is not fully reversible. When the difference in peak potential in the cathodic and anodic process is fitted versus the square root of the scan rate, a linear curve with an R^2 value of 98.2 % is obtained. Also the ratio of the peak currents approaches unity, especially at the higher scan rates. From these results, we concluded that the process is not irreversible and can be considered quasi-reversible.

To quantify the mass transport, the diffusion coefficient D of Cu^+ (with $[\text{Cu}(\text{MeCN})_4]^+$ as the diffusing complex) was measured by the Levich equation. This equation is applied in combination with experiments on a rotating disk electrode (RDE). The

Levich equation

$$j_L = 0.62nFD^{2/3}\nu^{-1/6}c\sqrt{\omega} \quad (2)$$

gives the relation between the limiting current density j_L (in A m^{-2}) and D (in $\text{m}^2 \text{s}^{-1}$) for different values of the rotation speed ω (in rad s^{-1}), with n the number of exchanged electrons (1), F the Faraday constant, c the concentration of copper ions (3100 mol m^{-3})¹⁷ and ν the kinematic viscosity ($5.7 \cdot 10^{-6} \text{ m}^2 \text{s}^{-1}$)¹⁷. A plot of j_L vs. $\sqrt{\omega}$ should be a straight line, with a slope proportional to $D^{2/3}$. Figure 3(a) shows potential scans in $[\text{Cu}(\text{MeCN})_4][\text{Tf}_2\text{N}]$: for potentials higher than 1.8 V, the current density is constant for a given rotation rate. The peaks that appear in the potential scans for rotation rates of 100 and 200 rpm are caused by the same mechanism that explains the appearance of peaks in cyclic voltammograms of non-stirred solutions: the interplay of a growing diffusion layer with time and an increasing concentration gradient with varying potential until the surface concentration of Cu^+ reaches zero, showing a maximum in the plot. At higher rotation rates this phenomenon is overruled by the better mass transport. This does not affect our further analysis, which is based only on the limiting currents. In figure 3(b), these limiting current densities j_L are plotted vs. $\sqrt{\omega}$ and the data can be perfectly fitted with a line through the origin. As explained above, the diffusion coefficient D can then be calculated from the slope of this fit and is equal to $1.0 \cdot 10^{-11} \text{ m}^2 \text{s}^{-1}$. This is a rather low value, especially when compared to aqueous solutions where diffusivities around $1.38 \cdot 10^{-9} \text{ m}^2 \text{s}^{-1}$ can be found for Cu^+ ions³³. An adequate mass transport thus requires forced convection for this system, but a good convective flow of the electrolyte is, however, a prerequisite for any RFB.

Charge-discharge experiments were performed in a commercially available closed H-type glass cell of two double-walled compartments, purchased from SES GmbH-Analytical Systems. Special care was taken to ensure the cell is properly sealed and free from oxygen and water as to not influence the speciation of the Cu^+ . Also, all seals must be resistant to acetonitrile. No further modifications to the H-type glass cell were necessary. The temperature was set by pumping water through the outer wall, of which the temperature was controlled by a standard laboratory heating bath. As electrodes, platinum coils were used, hence the exact surface area is unknown. The coils were however big enough so that the applied current density during charge-discharge was well below 0.2 A dm^{-2} . As the ion-selective membrane, a commercially available Morgan membrane was used. It was soaked in the electrolyte (which was diluted with MeCN to have a liquid at room temperature), thereby ensuring it contained enough $[\text{Tf}_2\text{N}]^-$ anions to carry the current: no degradation was observed over a period of weeks. Cycle experiments were started with a state-of-charge (SOC) of 5%. For this purpose, a pre-charging current of 2 mA was applied for 2 h. After this time, 9 cycles were recorded. A cycle consisted of charging for 1 h at 2 mA, consecutively followed by discharging (also at 2 mA) until the cut-off voltage of 0.0 V was reached. The evolution of the voltage is presented in figure 4(a). Because of the pre-charging, the first discharge only happened 3 h after starting the experiment. The voltage during

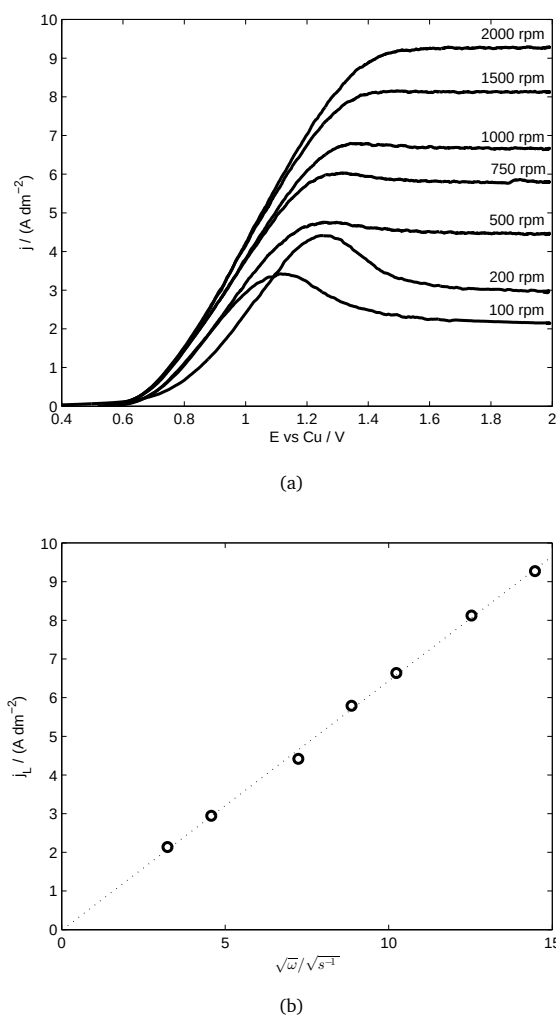


Fig. 3 (a) Potential scans at 90 °C with a scan rate of 20 mV s^{-1} at different rotation rates, (b) limiting current densities j_L at 2.0 V as a function of $\sqrt{\omega}$.

charge is around 1.35 V, while the discharge voltage is about 0.44 V. These values differ considerably from the expected voltage of 0.9 V. These differences are attributed to the Ohmic drop over the Morgane membrane. The Ohmic drop V_Ω was calculated by:

$$V_\Omega = \frac{i\Omega_m}{A} + \frac{il}{A\sigma} \quad (3)$$

where i is the charge/discharge current (in A), Ω_m the membrane area resistance (in $\Omega \text{ m}^2$), A the membrane surface area (in m^2), l the distance between the electrodes (in m) and σ the electrical conductivity of $[\text{Cu}(\text{MeCN})_4][\text{Tf}_2\text{N}]$ ($1.62 \Omega^{-1} \text{ m}^{-1}$)¹⁷. The membrane area resistance was determined by Electrochemical Impedance Spectroscopy. A value of $26 \Omega \text{ m}^2$ was obtained. The first term of equation (3) is the voltage drop over the membrane, the second term is the iR drop over the electrolyte. V_Ω is of the order of 0.4 V, what explains the large deviations from the expected 0.9 V during charging and discharging. The overpotentials required to drive the electrochemistry are small (see figure 2) and negligible compared to the potential loss over the membrane.

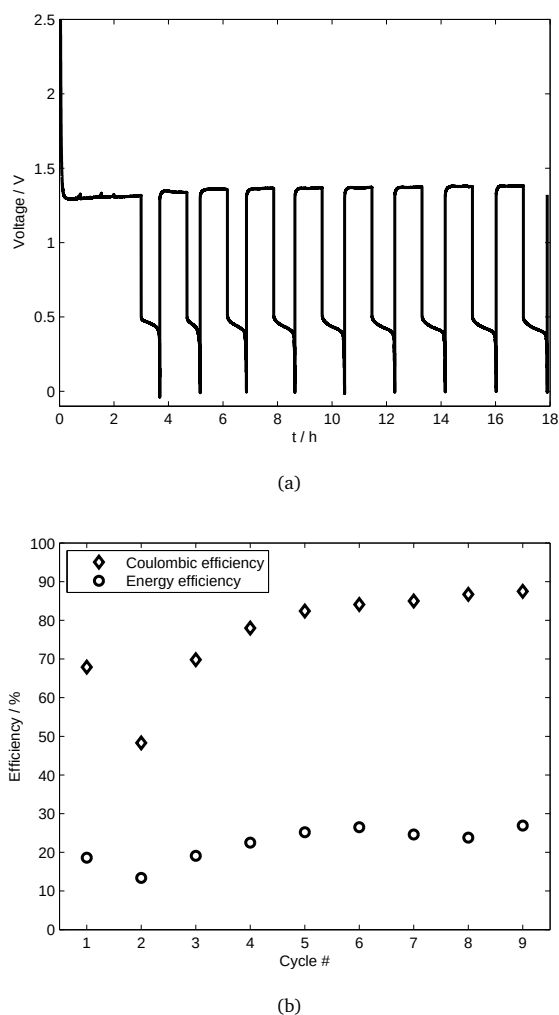


Fig. 4 Cycling in $[\text{Cu}(\text{MeCN})_4][\text{Tf}_2\text{N}]$ at $90\text{ }^\circ\text{C}$: (a) constant-current cycling curves; (b) Coulombic and energy efficiency.

Figure 4(b) shows the Coulombic and energy efficiency for the measured cycles. The Coulombic efficiency varies strongly during the first three cycles but remains higher than 80% from cycle 5 onward. This is in the higher end of reported Coloumbic efficiencies for non-aqueous RFBs^{4–6,8–10}. As there are no side-reactions possible in a liquid metal salt such as $[\text{Cu}(\text{MeCN})_4][\text{Tf}_2\text{N}]$, the deviation of 100% efficiency is attributed to detachment of copper dendrites from the electrode, making them unavailable during discharge and cross-over between the compartments. The energy efficiency varies between 10 and 30%. This is a low value, but in line with other reported energy efficiencies^{8,9} and it is mostly influenced by the poor electric conductivity of the Morgane membrane for the bistriflimide anions. Furthermore, as mentioned earlier, this low efficiency is mainly caused by the resistance of the membrane between the catholyte and anolyte compartment.

The liquid metal salt $[\text{Cu}(\text{MeCN})_4][\text{Tf}_2\text{N}]$ was evaluated as an electrolyte for RFBs. Liquid metal salts can act as solvent and electroactive species due to the metal ion that is incorporated into their molecular structure. The main advantage is the high con-

centration of ions and, hence, the high charge density of 300 kC l^{-1} . The redox couples Cu^+/Cu and $\text{Cu}^{2+}/\text{Cu}^+$ can be observed in $[\text{Cu}(\text{MeCN})_4][\text{Tf}_2\text{N}]$ and are separated by 0.9 V. An H-type glass cell with a Morgane membrane was used to characterize the charge-discharge properties of the compound. At a SOC of 5%, the Coulombic and energy efficiency were around 85% and 25%, respectively. The energy density is currently limited by the anion exchange membrane. Further studies are being performed to synthesize better membranes.

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