



## Description and performance of a novel aqueous all-copper redox flow battery



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### HIGHLIGHTS

- A novel, aqueous chemistry based on copper for use in redox flow cells is presented.
- Comparable energy density to vanadium systems due to high solubility of copper (3 M).
- Uses low cost, less toxic, easily recyclable and abundant materials.
- Simplicity: single step preparation of electrolyte and no catalysts required.
- Elimination of heat exchangers since the operational temperature range is extended.

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### ABSTRACT

In this paper we present a novel aqueous redox flow battery chemistry based on copper chloro complexes. The energy density ( $20 \text{ Wh L}^{-1}$ ) achieved is comparable to traditional vanadium redox flow batteries. This is due to the high solubility of copper (3 M), which offsets the relatively low cell potential (0.6 V). The electrolyte is cheap, simple to prepare and easy to recycle since no additives or catalysts are used. The stack used is based on plain graphite electrode materials and a low-cost microporous separator. The system can be operated at  $60^\circ\text{C}$  eliminating the need for a heat exchanger and delivers an energy efficiency of 93, 86 and 74% at 5, 10 and  $20 \text{ mA cm}^{-2}$  respectively.

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## 1. Introduction

The growing demand for electricity expected during the coming decades has increased interest in the development of new technologies for energy production from renewable power sources, such as wind and solar. However, the success of these new renewable power sources needs to be coupled with the introduction of competitive energy storage devices for load-levelling and peak-shaving such that these renewable sources could be tied to the grid. In this fashion, the problem of the unpredictable and intermittent energy production behaviour of renewable power sources may be overcome. For electrical energy storage,

electrochemical devices such as batteries and supercapacitors have been shown to provide higher efficiencies compared to other energy storage systems currently utilized [1,2].

Within the wide variety of electrochemical devices for energy storage, redox flow batteries (RFB) are one of the best options for massive storage due to their higher capacity for massive storage in comparison with other battery technologies. RFBs typically employ two soluble redox couples at high concentrations in aqueous or organic media which are stored in two external tanks and pumped into an electrochemical reactor, where one of the species of the redox couple is transformed into the other, storing or delivering energy depending upon whether the device is charging or discharging. The reactor is composed of a stack of two-electrode cells. The two electrodes are typically composed of graphite bipolar plates and carbon felts. These electrodes are separated by an ionic exchange membrane, typically Nafion, to avoid mixing of the positive and negative half-cell electrolytes [3].

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Many types of RFB have been widely explored since the first appearance of the Fe–Cr flow cell in 1973 [4], including hybrid systems and chemically regenerative redox fuel cells [1,2,5–7]. However, only the iron–chromium, all-vanadium (VRB), zinc–bromine and sodium–polysulfide (PSB) have come close to full-scale commercialization. At this point, the reduction of cost of the different materials employed in the electrodes, the membranes and the electrolyte is mandatory to promote the introduction of RFBs in the worldwide market.

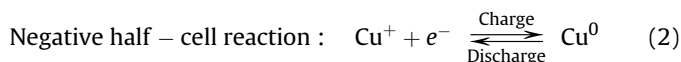
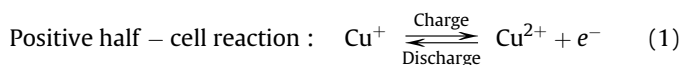
A feasible strategy to reduce the cost of RFBs is the total or partial substitution of the half-cell electrolytes of the RFB systems mentioned above by alternative redox couples. These alternative redox couples should be abundant, non-toxic and highly soluble in water. Ideally, they should provide a redox potential close to the anodic and cathodic limits of the operational potential window of the supporting electrolyte, which should be highly conductive and simple to recycle.

In this work, the redox processes of copper species are applied for the first time in an aqueous all-copper RFB, where the three oxidation states of copper are present in a hybrid redox flow configuration. The employment of the same element in both half-cells reduces the problem of cross-contamination across the membrane, allowing the use of simple and cheap microporous separators. All-copper redox batteries have been previously reported based on acetonitrile [8,9] ionic liquids [10] and deep eutectic solvents [11].

### 1.1. The all-copper system: redox reactions and potential

In previous studies [12], the degree in electrochemical reversibility of the Cu(I)/Cu(II) redox couple in chloride media at 1 M concentration of copper was investigated. It was found that the values of peak potential separations of this couple were comparable to those displayed by vanadium redox couples, showing a quasireversible behaviour. In addition, a noticeable displacement of the formal potential of the Cu(I)/Cu(II) redox couple towards much more positive values was observed, reaching the experimental potential displayed by the Fe(III)/Fe(II) redox couple, which has also been widely employed in flow cells, for instance in a hybrid all-iron configuration [13] and more recently in the Fe–V RFB [14–16].

In the all-copper RFB the chemistry of the Cu<sup>0</sup>–Cu(I)–Cu(II) system is employed to store and deliver electricity within the battery, as shown in Equations (1) and (2). The fresh electrolyte, which is initially composed by cuprous chloro complexes, is transformed into cupric chloro complexes in the positive half-cell and electro-deposited as copper on the negative electrode surface during charge. Therefore, during discharge, the cupric ions formed in the positive half-cell electrolyte are transformed again to Cu<sup>+</sup> ions, while the stripping of the copper deposit occurs in the negative side.



The potential difference between these two kinetically facile reactions in highly concentrated chloride media is around 0.7 V according to previous electrochemical studies of copper-chloride electrolytes in aqueous or deep eutectic solvents [11,12].

### 1.2. Economic and technological potential of the all-copper system

The cell potential of the all-copper system is low compared to RFB chemistries typically used, such as the well-known all-

vanadium or Zn–Br systems [1,2,5,6]. However, as this paper will show, the excellent kinetics and the simplicity (no catalyst or ion-exchange membrane required) of the all-copper system coupled with the high concentrations of electroactive species that can be achieved in aqueous media, make this system equally attractive in terms of energy density, energy efficiency and cost per Wh stored. The relatively low power density of the all-copper system is not an insurmountable problem from an economic point of view. The simplicity and the low cost of the materials employed can be expected to offset at least part of the cost of a larger stack. For example, the combined cost of Nafion membranes and vanadium used in a typical all-vanadium RFB is over half the system cost [17]. In the all-copper system the use of simple and cheap nanoporous composite separators, which typically cost 20 to 100 times less than ion exchange membranes [Amersil S.A., personal communication, September 2013] is possible.

Due to the relatively small cell potential the redox processes shown in Equations (1) and (2) are both favoured over the chlorine and hydrogen evolution processes, therefore no gas evolution is likely within this system. This is an important simplification and both eliminates the need for electrolyte balancing mechanisms and safely allows deeper cycling over the entire SOC. Crucially, compared to the dominantly used element, vanadium, copper is abundant, less toxic and can be obtained at extremely high purity at lower cost. Due to the use of three oxidation states preparation of electrolytes is also trivial. In the discharged state the electrolytes in both half-cells are identical and these can be prepared by simply reacting an electrolyte containing any ratio of Cu(II) to Cu(I) with Cu<sup>0</sup>. In addition, no catalysts are required since the kinetics of the reactions are impressive on carbon materials. Finally, the heat exchanger of the vanadium system is eliminated since no complications with the stability of the electrolytes was found over a wide range of temperature, from 5 to 70 °C.

The electrolytes can be readily recycled in widespread industrial processes such as electrowinning [18], Hydrocopper<sup>®</sup> [19] or copper etching [20]. Therefore, the initial investment in the electrolyte can be easily recovered at the end of the life of the battery.

## 2. Experimental

### 2.1. Electrolyte preparation

The Cu(I) electrolyte used to fill both storage tanks was prepared from Cu(I) chloride (>99% purity, Acros Organics) salt. The concentration of copper was varied from 1 M up to 3 M in the different cycling tests. In order to increase the concentration of chloride, calcium chloride (>95% purity, Scharlau) and HCl (37% Panreac) were utilized as mixed supporting electrolyte in both half-cells. The respective concentrations of acid and salt were the same in all the solutions; 2 M and 4 M of each in the electrolytes at 1 M and 3 M copper concentration respectively. Cuprous ions are easily oxidized by oxygen so the solutions were stirred with mild heating in contact with metal turnings (Fluka, >99.0%) until they became completely colourless, in order to reduce all the cupric ions that could be formed during the preparation of the electrolytes. However, no further procedures are required in the preparation of the electrolytes.

### 2.2. Cell assembly

The single flow cell was built using a sandwich type flow reactor (Micro Flow Cell, Electrocell) with graphite electrodes of 10 cm<sup>2</sup> active area in both half-cells. A platinum wire pseudo reference electrode was placed in the positive half-cell in order to record the overpotentials of each electrode separately. Stainless steel and

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