

Supporting Information

Removal of copper from water using a thermally regenerative electrodeposition battery

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Electrode potential calculations

The Nernst equation for calculating cathode and anode electrode potential:

$$E = E^0 - \frac{RT}{2F} \ln \frac{1}{\alpha(Cu^{2+})} \quad (S1)$$

$$E = E^0 - \frac{RT}{2F} \ln \frac{[\alpha(NH_3)]^4}{\alpha(Cu(NH_3)_4^{2+})} \quad (S2)$$

where E^0 is the standard reduction potential of either cathodic or anodic reaction, R is the gas constant ($J K^{-1} mol^{-1}$), T is the solution temperature (K), F is the Faraday constant ($96485 C mol^{-1}$), and $\alpha(Cu^{2+})$, $\alpha(NH_3)$, $\alpha(Cu(NH_3)_4^{2+})$ are the activities of copper ion, ammonia, and copper complex, respectively.

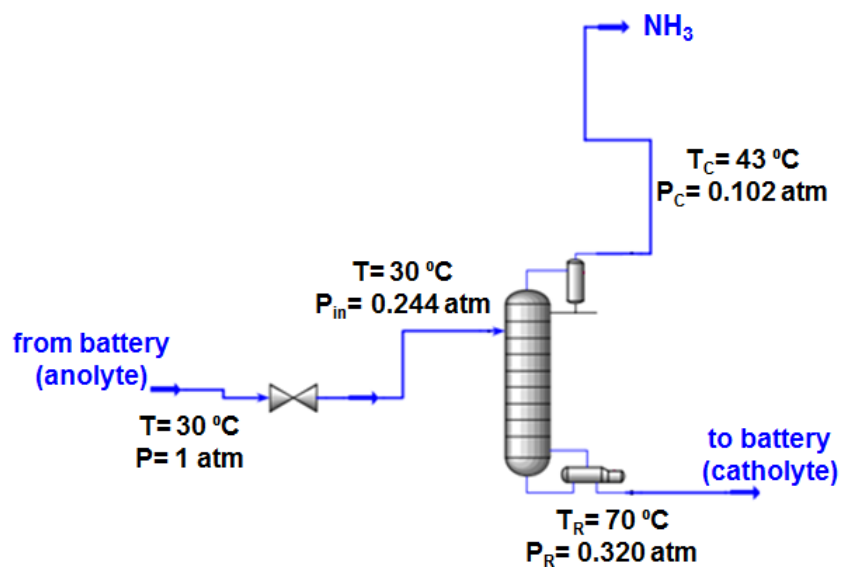


Figure S1. Schematic of the distillation column for ammonia separation from the anolyte (charge the battery).

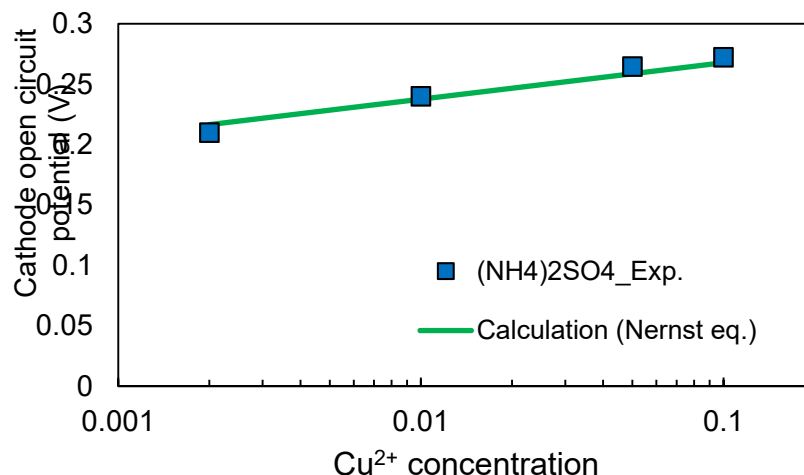


Figure S2. Cathode open-circuit potential at different copper concentrations with $(\text{NH}_4)_2\text{SO}_4$ as the supporting electrolyte, compared to those estimated by using Nernst equation.

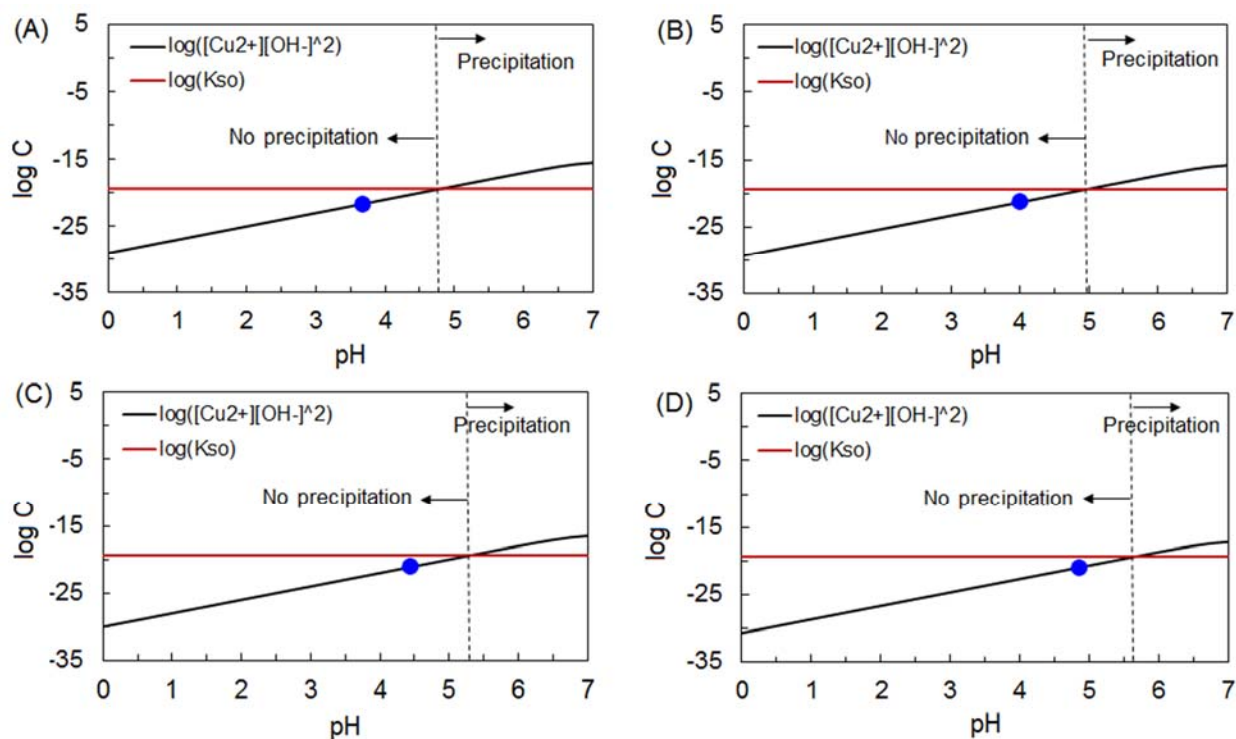


Figure S3. Initial states of catholyte (blue points) with 1 M $(\text{NH}_4)_2\text{SO}_4$ supporting electrolyte, and (A) 0.1, (B) 0.05, (C) 0.01, and (D) 0.002 M Cu(II). The vertical axis (log C) shows either $\log ([\text{Cu}^{2+}] \times [\text{OH}^-]^2)$ (black line) or $\log K_{s0} = -19.36$ (red line). Precipitation occurs at the point where $\log ([\text{Cu}^{2+}] \times [\text{OH}^-]^2)$ is higher than the solubility constant of $\text{Cu}(\text{OH})_2$ [$\log K_{s0} = -19.36$]. The initial states of the catholytes (blue points) are all below the red line, showing all the initial Cu(II) was present in the aqueous phase.

Based on the below calculation, we conclude that the pale blue precipitates that formed in the solution containing 0.002 M Cu(II) were Cu(OH)₂. For other concentrations, formation of precipitates was not thermodynamically possible ($\log Q < \log K_{s0}$).”

Table S1. Copper ion and hydroxide concentrations for calculating the possibility of Cu(OH)₂ precipitation formation

Initial Cu(II) concentration (C _i ; M)	Final catholyte pH	Final OH ⁻ concentration (M)	Cu(II) removal (Rem; %)	Final Cu(II) concentration (C _f ; M) *	log Q **
0.1	5	10 ⁻⁹	63	3.70×10 ⁻²	-19.43
0.05	5.2	1.59×10 ⁻⁹	77	1.15×10 ⁻²	-19.54
0.01	5.4	2.51×10 ⁻⁹	48	5.20×10 ⁻³	-19.48
0.002	5.9	7.94×10 ⁻⁹	2	1.96×10 ⁻³	-18.91

* Calculated as $C_f = C_i (1 - \text{Rem}/100)$;

** Calculated as $\log Q = \log([Cu^{2+}] \times [OH^-]^2)$. The Cu(OH)₂ precipitations form when log Q is higher than log K_{s0} which is -19.36;

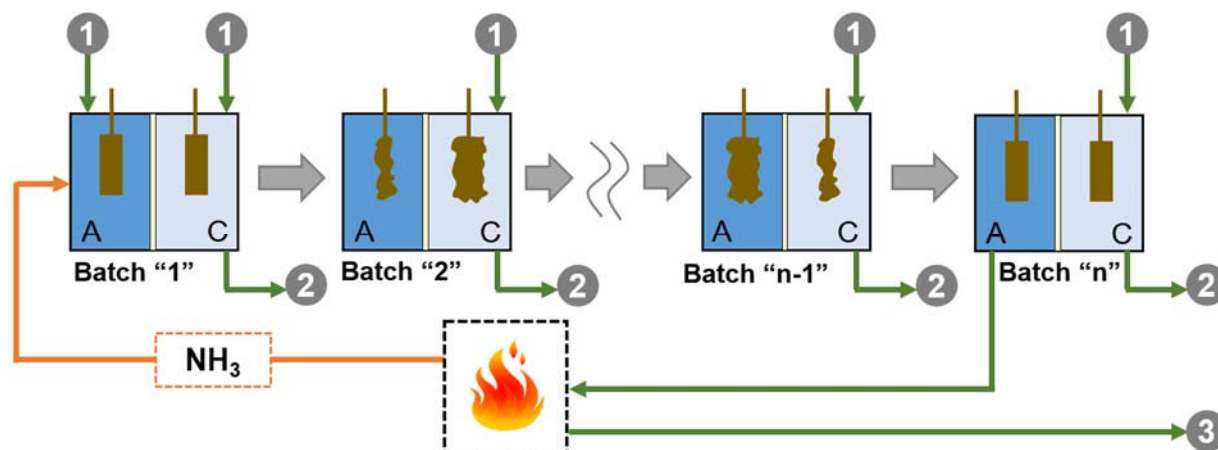


Figure S4. An example of the TREB process used as a treatment system. To minimize the volume of the anolyte produced, the solution in the anode compartment could remain in the chamber for several batches of fresh catholyte, so that the catholyte is replaced by a new copper solution for each of “n” batches. As shown in the figure, when the copper removal from the catholyte is reduced due to reduced performance of the anolyte, and power production is low (batch “n”), the anolyte is regenerated using waste heat, and ammonia is added to a new anolyte. The lines labeled with “1” indicate that the reactor chamber would be filled with a fresh copper-containing solution. The lines labeled with “2” indicate the removal of the treated effluent with a decrease Cu concentration. The line labeled with “3” represents the high concentration effluent that could be used for copper recovery. The letter “A” is used for anode chamber, while “C” indicates the cathode. In the separation unit, ammonia is separated from the high concentration effluent, and is added to the first batch reactor. In order to regenerate the electrodes, after each batch, the electrodes were switched.