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Using Li^+ as the electrochemical messenger to fabricate an aqueous rechargeable Zn-Cu battery

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Experimental section

CV curves for Cu electrode were traced on Chenhua 660D electrochemistry workstation at a scan rate of 0.01 V s^{-1} using a piece of natural graphite brush as the work electrode, Pt electrode as the counter and a saturated calomel electrode (SCE) as the reference. The electrolyte was prepared by carefully adding 0.1 mol L^{-1} $CuSO_4$ aqueous solution into 1 mol L^{-1} Li_2SO_4 aqueous solution. Note that the density of $CuSO_4$ solution is high than that of Li_2SO_4 and thus sinks to the bottom of the container. As a result, the solution was kept in two layers. Then the counter and the reference were carefully dipped to the bottom of the solution and the graphite brush was kept touching the $CuSO_4$ layer slightly across the Li_2SO_4 layer. The CV curve for Zn electrode was carried out in the same way.

The Zn-Cu batteries were fabricated as follows. The cathode aqueous electrolyte was composed of $CuSO_4$ mixed with Li_2SO_4 with a concentration of 0.1 mol L^{-1} and 1 mol L^{-1}, respectively, using a piece of polished copper as the current collector. 0.1 mol L^{-1} $ZnSO_4$ mixed with 1 mol L^{-1} Li_2SO_4 aqueous solution was used as the anode, a piece of polished zinc as the anode current collector. All solutions were washed by N_2 flow for 30 minutes prior to tests. A piece of sandwiched membrane was employed as the separator which had been reported in former studies.[1] A mixture of $LiClO_4$ and PMMA (polymethylmethacrylate) in N-methyl-2-pyrrolidone (NMP) solution was cast on a porous PVDF (poly(vinylidene fluoride) film. The mass ratio of $LiClO_4$ and PMMA is about 1:10. After dried at 75 °C in vacuum, another layer of the porous PVDF film was covered on the PMMA layer. Then the membrane was tailored into a disk with a thickness of about 0.2 mm. SS-Cu and Zn-C systems were constructed in the same way with Zn-Cu battery, by using stainless steel replacing the Zinc electrode or the carbon brush replacing the copper electrode, respectively.

The impedance spectra in the frequency range of 0.01 Hz–100 kHz was characterized using zinc as the work electrode and copper as the counter. The excitation voltage was 10 mV. The charge-discharge curves and cycle calendar life were traced on a cell tester (Neware) between 0.5–1.5 V. All of the characterizations were collected at room temperature. An *ex-situ* ICP-AES examination was performed to study the concentration of Cu^{2+} and Li^+ swung with charge and discharge process. Four Zn-Cu batteries that obtained almost the same contents were fabricated and performed at various charge-discharge depths. Then the electrodes were taken out and the left electrolytes were subjected to the ICP-AES. Scanning electron microscope (SEM) images of the samples were collected on a JSM-6360LA. Conventional powder XRD patterns were carried out in the 10–80^o 2θ range using a D/max 2500 PC with vertical goniometer and Cu Kα radiation (λ=1.5406 Å).

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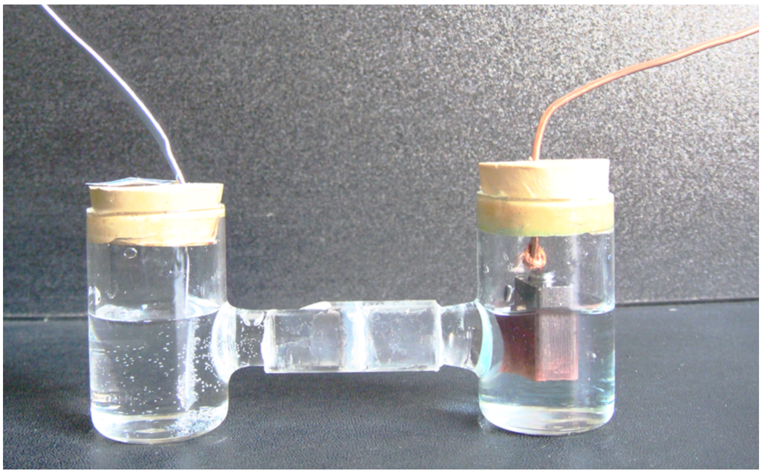

Fig. S1 The Zn|$ZnSO_4$ + Li_2SO_4|ion-block membrane|$CuSO_4$ + Li_2SO_4|Carbon system.

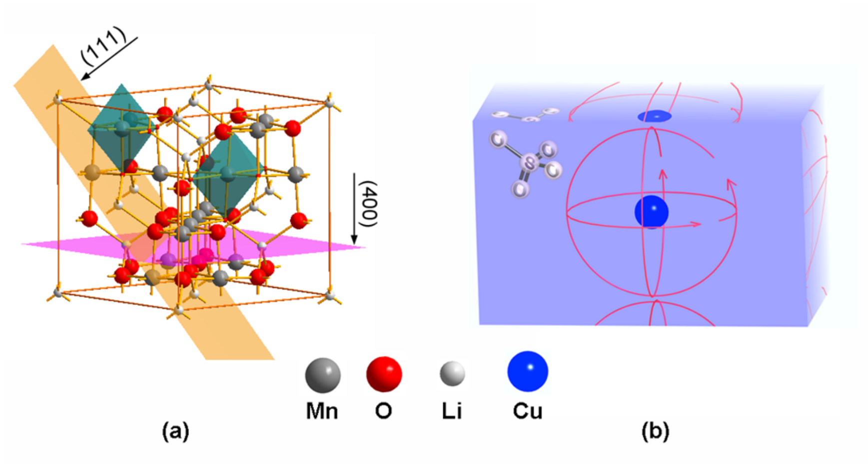

Fig. S2 The chemical surroundings of (a) the Mn^{3+}/Mn^{4+} active centre in $LiMn_2O_4$ crystal lattice and (b) Cu^{2+} in $CuSO_4$ aqueous solution.

The capacity loss for materials in solid state might be different with materials in liquid state. In the Zn-Cu system, the practical capacity is 98.5% of the theoretical capacity. This result is notable since the practical capacities for most of the active materials in solid state are much lower than their theoretical capacity.[1–6] The capacity loss for materials in solid state might be ascribed to the steric hindrance that prohibits the free rotation of the active interface to the right direction, leading to the decrease of the capacity, as illustrated in Fig. S2. In the case of $LiMn_2O_4$, facet (111) is superior, although enhancing facet (400) is helpful for the intercalation/de-intercalation of Li^+, the Mn^{3+}/Mn^{4+} active centre is still confined in the crystal lattice which indicates Mn^{3+}/Mn^{4+} redox couple can not receive-release the electrons freely.[7] In the case of $CuSO_4$ in aqueous solution however, no steric hindrance holds back the movement of the Cu^{2+} active centre. As a result, the active ions can move and rotate freely to the right location and right direction to accept or release electrons, which certainly helps to elevate the capacity.

References

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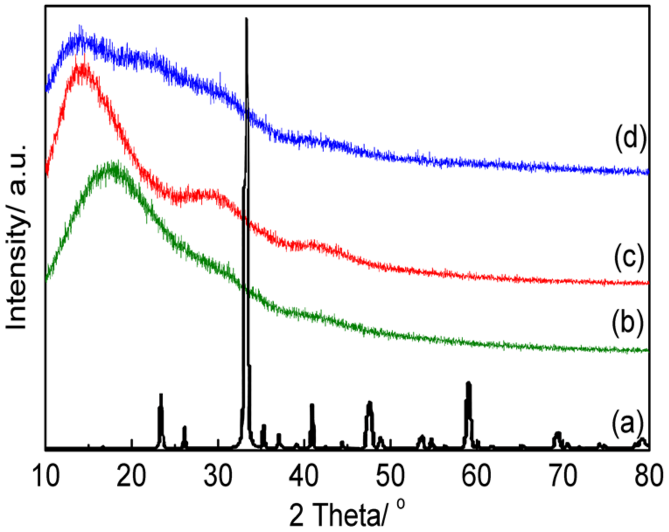


Fig. S3 XRD patterns of the contents of the PVDF/PMMA-LiClO$_4$/PVDF sandwiched ion-block membrane. (a) LiClO$_4$. (b) PMMA. (c) PMMA mixed with LiClO$_4$ before cycling, and (d) The PMMA-LiClO$_4$ inner layer after 332 cycles with the outer PVDF layers being peeled off.

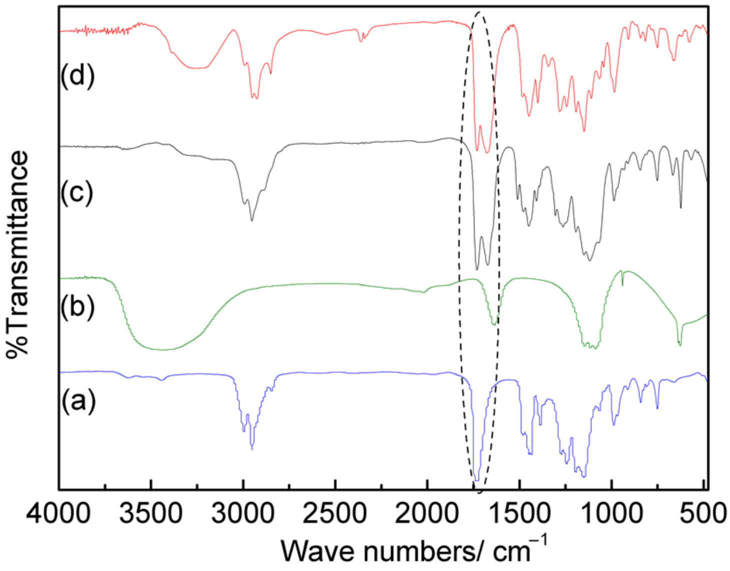


Fig. S4 FTIR of the contents of the PVDF/PMMA-LiClO$_4$/PVDF sandwiched ion-block membrane. (a) PMMA. (b) LiClO$_4$. (c) The original PMMA-LiClO$_4$ film, and (d) The PMMA-LiClO$_4$ inner layer after 332 cycles with the outer PVDF layers being peeled off.

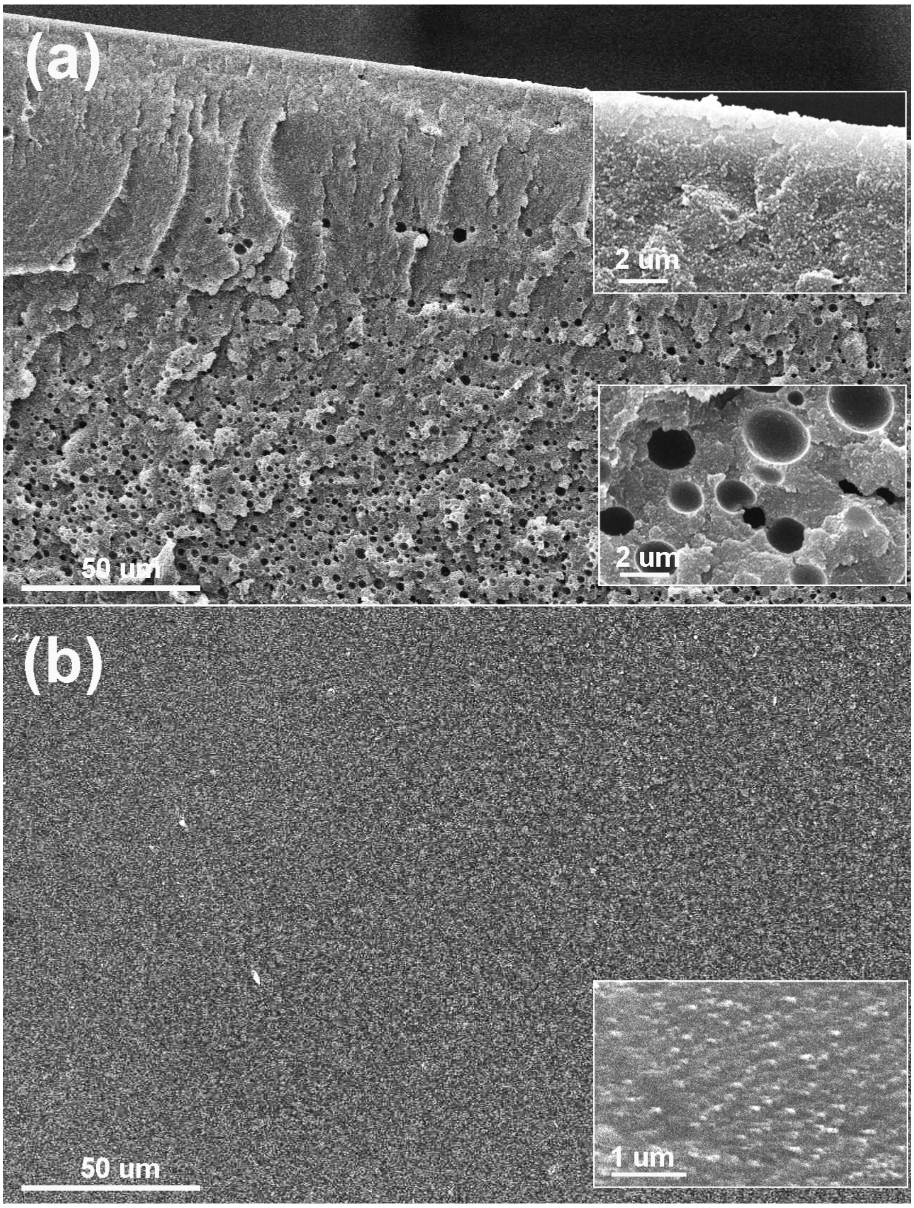


Fig. S5 SEM of (a) the section and (b) the surface of the PVDF/PMMA-$LiClO_4$/PVDF sandwiched ion-block membrane after 332 cycles with the outer PVDF layers being peeled off.

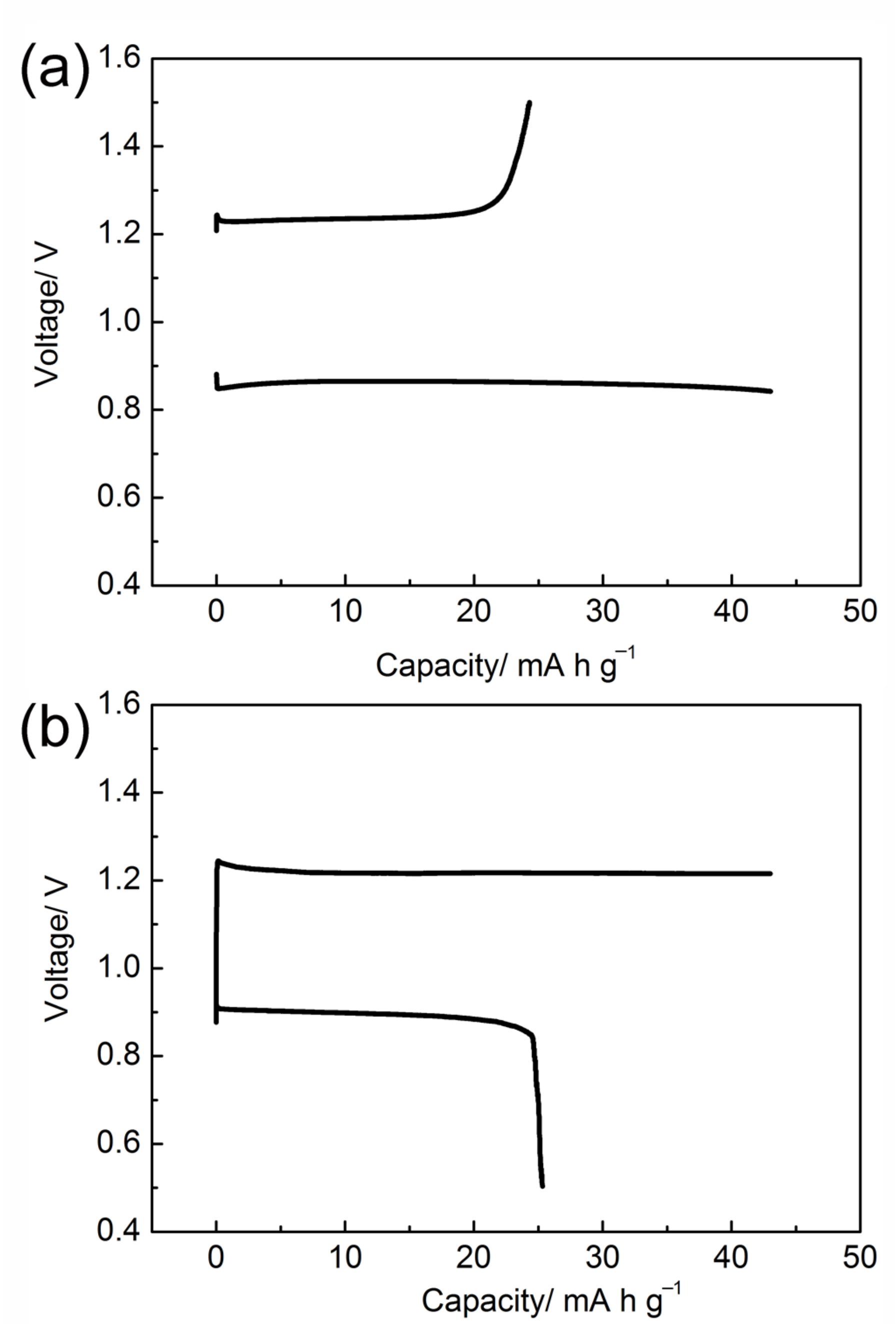


Fig. S6 Charge-discharge curves of (a) Zn-C and (b) SS-Cu systems at a current density of 6 mA cm^{-2}.

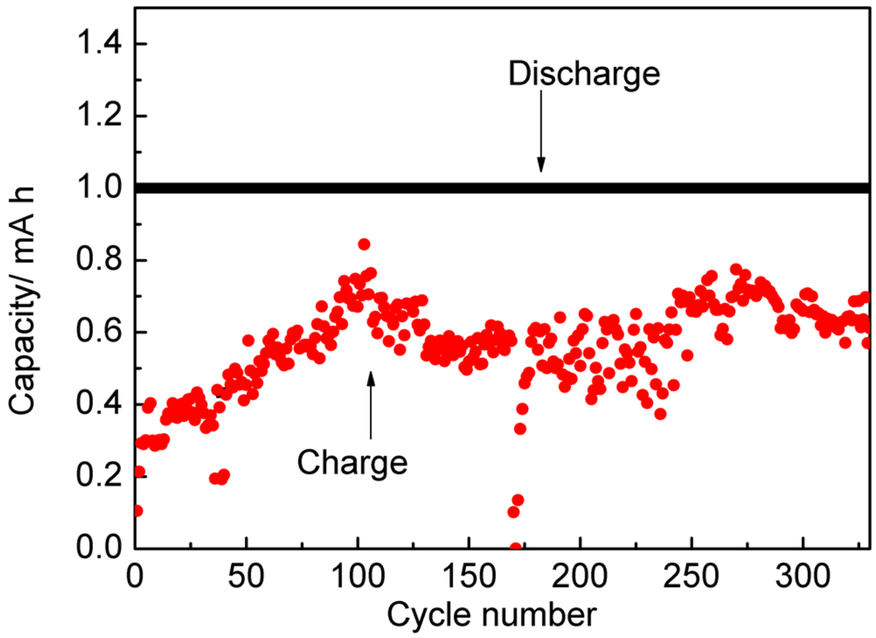


Fig. S7 Cyclic performance of Zn-C system. The discharge capacity is controlled at 1 mA h.

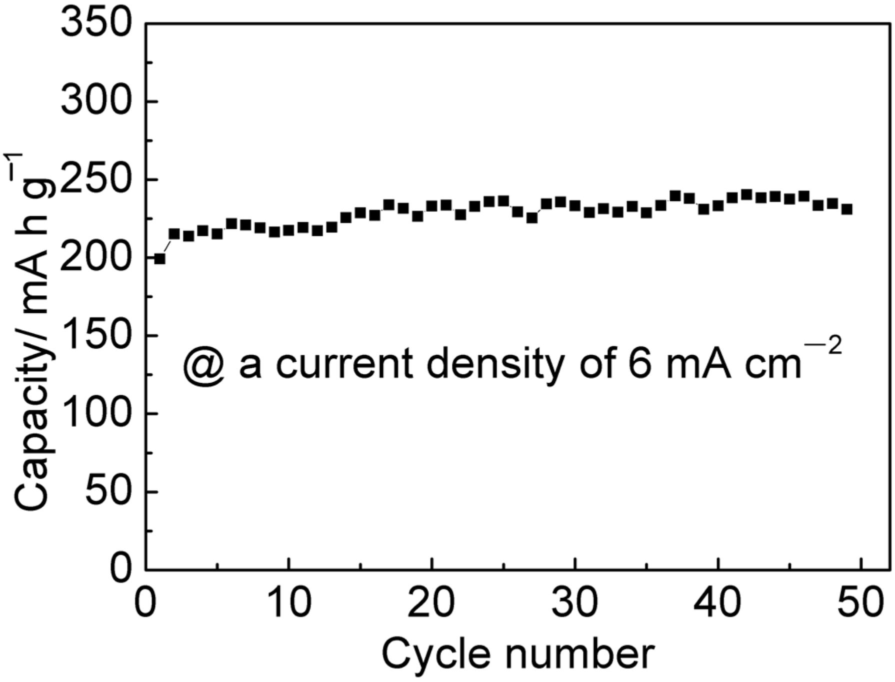


Fig. S8 Cyclic performance of the Zn-Cu system based on the capacity of $CuSO_4$. The current density is calculated according to the area of the membrane that the current passes through.

Calculation of the theoretical capacity for $CuSO_4$

The calculation is based on the following equation:

$$C = Q/M \quad (1)$$

where C is the capacity, Q corresponds to the quantity of electricity carried by per mole of $CuSO_4$ in unit time, and M is the molecular weight.

Then, after unit conversions,

$$C = 2 \times 1.602 \times 10^{-19} \times 6.02 \times 10^{23} \div 3600 \div 159.61 \times 1000 = 336 \text{ mAh g}^{-1} \quad (2)$$

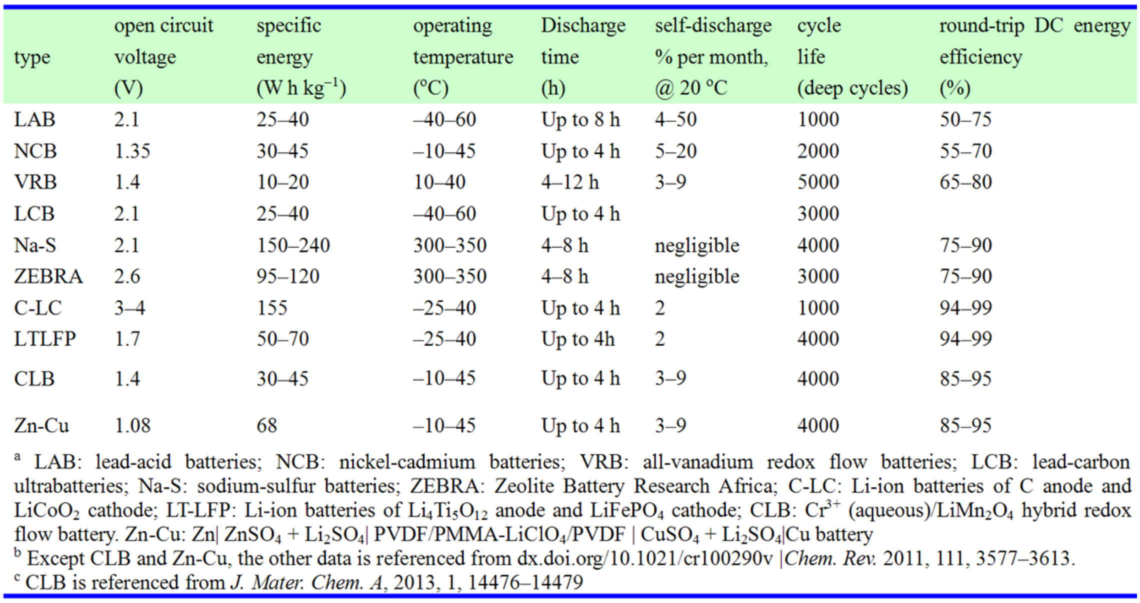
In our work, the practical capacity based on $CuSO_4$ is up to 330 mA h g^{-1} at a current density of 1 mA cm^{-2}, which is 98.5% of the theoretical capacity without considering the concentration of the aqueous solution. Here we intend to disclose that almost all of the $CuSO_4$ in the solution has been involved in the electrochemical reaction, which is different from most of solid active materials. When the concentration of the aqueous solution is taken into consideration, the theoretical capacity of $CuSO_4$ would be as follows:

$$C = 2 \times 1.602 \times 10^{-19} \times 6.02 \times 10^{23} \div 3600 \div 159.61 \times 1000 \times 20.5\% = 69 \text{ mAh g}^{-1} \quad (3)$$

Here the concentration of the $CuSO_4$ in aqueous solution is about 20.5 wt% at 20 ^{o}C (according to Lange's Handbook of Chemistry, 15th Edition). However, the practical capacity would still be 98.5% of the theoretical capacity.

On the other hand, if the calculation is carried out according to the mass of $ZnSO_4$, the anode material in aqueous solution, the theoretical capacity would be 332 mAh g^{-1}. When the concentration of 53.8 wt% at 20 ^{o}C is accounted (according to Lange's Handbook of Chemistry, 15th Edition), the theoretical capacity would come to be 179 mAh g^{-1}. In either case, the practical capacity would be 98.5% of the theoretical capacity.

Table S1. Technology Comparison of Potential Batteries[a] for Utility Applications[b, c]



type	open circuit voltage (V)	specific energy (W h kg^{-1})	operating temperature (°C)	Discharge time (h)	self-discharge % per month, @ 20 °C	cycle life (deep cycles)	round-trip DC energy efficiency (%)
LAB	2.1	25–40	–40–60	Up to 8 h	4–50	1000	50–75
NCB	1.35	30–45	–10–45	Up to 4 h	5–20	2000	55–70
VRB	1.4	10–20	10–40	4–12 h	3–9	5000	65–80
LCB	2.1	25–40	–40–60	Up to 4 h		3000	
Na-S	2.1	150–240	300–350	4–8 h	negligible	4000	75–90
ZEBRA	2.6	95–120	300–350	4–8 h	negligible	3000	75–90
C-LC	3–4	155	–25–40	Up to 4 h	2	1000	94–99
LTLFP	1.7	50–70	–25–40	Up to 4h	2	4000	94–99
CLB	1.4	30–45	–10–45	Up to 4 h	3–9	4000	85–95
Zn-Cu	1.08	68	–10–45	Up to 4 h	3–9	4000	85–95

[a] LAB: lead-acid batteries; NCB: nickel-cadmium batteries; VRB: all-vanadium redox flow batteries; LCB: lead-carbon ultrabatteries; Na-S: sodium-sulfur batteries; ZEBRA: Zeolite Battery Research Africa; C-LC: Li-ion batteries of C anode and $LiCoO_2$ cathode; LT-LFP: Li-ion batteries of $Li_4Ti_5O_{12}$ anode and $LiFePO_4$ cathode; CLB: Cr^{3+} (aqueous)/$LiMn_2O_4$ hybrid redox flow battery. Zn-Cu: Zn| $ZnSO_4$ + Li_2SO_4| PVDF/PMMA-$LiClO_4$/PVDF | $CuSO_4$ + Li_2SO_4|Cu battery

[b] Except CLB and Zn-Cu, the other data is referenced from dx.doi.org/10.1021/cr100290v |*Chem. Rev.* 2011, 111, 3577–3613.

[c] CLB is referenced from *J. Mater. Chem. A*, 2013, 1, 14476–14479

Calculation of the specific energy of the aqueous rechargeable Zn-Cu Daniell-type battery

(a) The theoretical specific energy (with the ideal concentration of 100 wt% for the electrode, i.e., water is neglected at the state of 100% DOD)

$$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu \quad (4)$$

$$W = V \times 1000 / (Q^+ + Q^-)\ (W\ h\ kg^{-1}) \quad (5)$$

Where W, V, Q^+ and Q^- represents energy density, open-circuit voltage, electrochemical equivalence of the cathode and electrochemical equivalence of the anode, respectively.

For this system,

$$V = 1.08\ V. \quad (6)$$

$$Q^+ = M_{CuSO_4} / (26.8 \times 2) \quad = 159.61 / (26.8 \times 2) = 2.98\ g\ (A\ h)^{-1} \quad (7)$$

$$Q^- = M_{Zn}/ (26.8 \times 2) = 65.38 / (26.8 \times 2) = 1.22\ g\ (A\ h)^{-1} \quad (8)$$

As a result, $W = 1.08 \times 1000 / (2.98 + 1.22) = 257\ W\ h\ kg^{-1}$

(9)

(b) The expected specific energy (with an aqueous concentration of 20.5 wt% for the cathode $CuSO_4$)

$Zn + CuSO_4$ (aqueous) → $ZnSO_4$ (aqueous) + Cu (10)

The formula is:

$W = V \times 1000 / (Q^+ + Q^-)$ ($W\ h\ kg^{-1}$) (11)

Where,

$V = 1.08$ V (12)

$Q^+ = M_{CuSO_4} / (26.8 \times 2 \times 14\%) \quad = 159.61 / (26.8 \times 2 \times 20.5\%) = 14.53$ g $(A\ h)^{-1}$ (13)

$Q^- = M_{Zn} / (26.8 \times 2) = 65.38 / (26.8 \times 2) = 1.22$ g $(A\ h)^{-1}$ (14)

As a result,

$W = 1.08 \times 1000 / (14.53 + 1.22) = 68$ W h kg^{-1} (15)