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ARTICLE TYPE

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

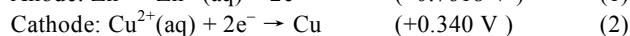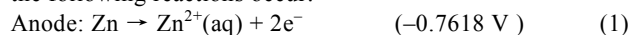**Hanping Zhang,* Tao Yang, Xin Wu, Yisen Zhou, Chao Yang, Tian Zhu and Rulin Dong**
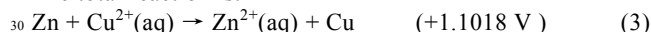
We propose an aqueous rechargeable Zn-Cu Daniell-type battery. In this system, Li$^+$ prefers to conduct currents rather than react with the electrodes, while the Zn-Cu electrode couples engage in their electrochemical reactions free from
10 **conducting currents. Here Li$^+$ performs like a messenger and thus could be called the electrochemical messenger.**

In biochemistry, molecular biology or neurobiology, chemical messengers such as neurotransmitters, messenger RNA and pheromone are used to disseminate information between or in
15 organic bodies.[1–3] Here we show that the behavior of the supporting electrolyte such as Li$^+$ in an electrochemical battery system is in accordance with this messenger model.

Zn-Cu Daniell-type battery is a classical electrochemical system which was firstly proposed by Daniell in 1830s. In a
20 typical demonstration form of Daniell cell, copper and zinc electrodes are immersed in an aqueous solution of $CuSO_4$ and $ZnSO_4$, respectively, using a salt bridge such as KCl aqueous support electrolyte saturated in gelatin or a porous barrier to connect the two solutions to conduct ions in the inner circuit.
25 When Cu and Zn electrodes are connected in the outer circuit, the following reactions occur:

Anode: $Zn \rightarrow Zn^{2+}(aq) + 2e^-$ (–0.7618 V)   (1)
Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu$ (+0.340 V)   (2)
The total reaction is:
30 $Zn + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu$ (+1.1018 V)   (3)

During the above mentioned discharge process, SO_4^{2-} moves from the cathode to the anode via the salt bridge and the Zn^{2+} moves in the opposite direction to maintain neutrality. Recharging the cell is difficult since Zn^{2+} would
35 move back together with Cu^{2+}, and this cross-over contamination reduces the reusability of the battery. Since 1860s, the Daniell-type cells had been supplanted in commercial applications by lead-acid rechargeable batteries. Nowadays, Daniell cell is only shown in classroom in middle
40 school due to its simplicity.

However, Zn and Cu electrodes are easy to be prepared and Zn-Cu battery is facile to be fabricated. In addition, the safety advantage brought by the employment of aqueous solutions used as the electrolyte is greatly enhanced, and the safety
45 issue has been one of the main drawbacks for a lithium ion battery to broaden its market towards large-scale applications such as vehicles and energy-storage domain.[4–12] In our modern energy-based, environment-concerned society,
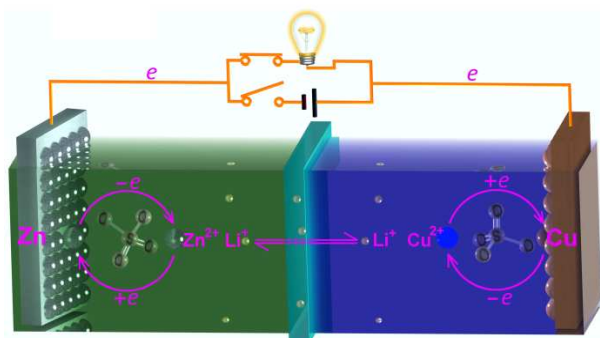
rechargeable Zn-Cu Daniell-type battery would be a strong
50 candidate for energy storage to back up the harvest of renewable energy coming from solar, wind and ocean.[13–17]

Virkar group has discussed the possibility of recharging the Daniel cell at 100 °C. Recently Xia group investigated the cell at room temperature.[18,19] These studies demonstrated that Zn-
55 Cu Daniell-type battery could be successfully cycled. In a traditional Daniell battery however, Zn^{2+} and Cu^{2+} act as the supporting electrolytes, while in a rechargeable battery, these cations would perform as active materials, which indicate that the rechargeable Zn-Cu battery involves reactions between
60 liquid electrodes of Zn^{2+} and Cu^{2+} in aqueous solutions and solid electrodes of metal zinc and copper. The novel role for aqueous cations in this system has not been well disclosed.

In an electrochemical cell, electrode active materials can be in solid, liquid or even gas state.[20–25] With the development of
65 solid electrolyte and ion exchange membrane,[26–30] electrochemical systems made of liquid electrodes have been widely investigated due to their flowability, safety and easy fabrication in large-scale applications.[31] Goodenough group presented the next generation of liquid cathode for lithium ion
70 batteries.[32,33] Zhou group combined aqueous solution with nonaqueous solution to construct rechargeable Ni-Li battery.[34] Recently, Zhao etc. proposed a Li-I hybrid redox battery with high output voltage.[35] These studies offer extraordinary effects of soluble electrodes.

75 In view of the growing investigation of soluble electrodes in new electrochemical technology, a clearer understanding of the interaction between the soluble electrode and the solid electrode would seem to be desirable. In this study, we fabricate a rechargeable Zn-Cu battery to investigate these
80 interactions. In this system, the solid electrode of Zn and Cu reacts with its own soluble electrode, respectively, while Li$^+$ shuttles to conduct charges rather than react with the electrodes and thus links the anode and the cathode together. Here the function of Li$^+$ is very like the chemical messengers
85 such as mRNA in protein syntheses and Ca^{2+} in nerve conductions. We thereby suggest using the electrochemical messenger (ECM) model to describe the work mechanism of the electrochemical systems that are in associated with the reaction between soluble electrode and solid electrode.
90 Compared with the well known rocking chair model for lithium ion battery,[36,37] the ECM model would perform better in disclosing the empirical unification between

electrochemical systems and the biochemical bodies.

Fig. 1 Schematic fabrication of an aqueous rechargeable Zn-Cu Daniell-type battery using Li^+ as the electrochemical messenger.
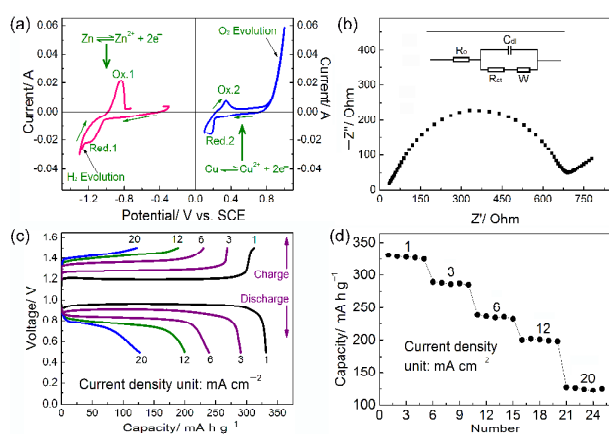
Fig. 2 Electrochemical performances of the Zn-Cu system. (a) Cyclic voltammetry (CV) behaviors of Zn and Cu electrodes in aqueous solutions at a scan rate of 10 mV s^{-1}. (b) Nyquist plot of the system. The inset is the equivalent circuit. (c) The charge-discharge curves and (d) The cycle performance at various rates based on the capacity of CuSO$_4$.

Fig. 1 illustrates the fabrication of the system. A piece of zinc and copper was dipped into ZnSO$_4$+Li$_2$SO$_4$ and CuSO$_4$+Li$_2$SO$_4$ aqueous solution, respectively. Ion-block type separator made of PVDF/PMMA-LiClO$_4$/PVDF sandwiched membrane was employed to conduct Li$^+$ ions, blocking other cations and anions from crossing over simultaneously.[38] When the system is discharged, electrons depart from zinc electrode and travel through the outer circuit to the counter electrode. The zinc electrode that loses electrons changes into Zn^{2+} and dissolves into the aqueous solution, thus increases its concentration. However, the extra Zn^{2+} can not pass through the ion-block membrane. As compensation, Li$^+$ ions pass through to the copper side to balance the cations. And when Li$^+$ arrives at the copper side, the total concentration of cations composed of Li$^+$ and Cu^{2+} is elevated. As a response, Cu^{2+} deposits to the current collector and harvests electrons coming from the outer circuit to change into copper. All of the processes are driven by the electrochemical potential difference between the couples of Zn^{2+}/Zn and Cu^{2+}/Cu,

spontaneously. Here Li$^+$ performs like a messenger which is sent by the potential of the system from the Zn side to the Cu side during discharging.

When the system is charged, the electrochemical potential difference between the couples of Zn^{2+}/Zn and Cu^{2+}/Cu is diverted artificially, which forces the electrons to depart from the copper electrode side, go back to the zinc side through the outer circuit, and Cu^{2+} dissolves into the cathode electrolyte, simultaneously. In this case, Li$^+$ is sent back by the electrochemical potential from the cathode side to the anode side like a messenger. As a response, Zn^{2+} bands together with the electrons on the current collector and the whole system recovers itself again.

On the whole, when the system operates Li$^+$ travels between the cathode and anode as an ECM to coordinate the behaviors of Zn^{2+} and Cu^{2+}. Recently, novel electrochemical systems such as PbSO$_4$//LiMnO$_2$, Zn//Na$_{0.95}$MnO$_2$ and Li//LiCoO$_2$ have been proposed.[39–41] And the ECM model is well in accordance with these systems which use Li$^+$ or Na$^+$ as a charge balance.

Fig. 2a exhibits the voltammetric behaviors of Zn and Cu electrodes in aqueous solutions, respectively. Obviously, both of the electrochemical reactions are reversible.[42] In a traditional Zn-Cu Daniell-type battery however, Cu^{2+} and Zn^{2+} cations conduct charges as well as participate the electrode reactions. As a result, the cross-over of the cations can hardly be circumvented. In the case of the ECM modeled system, Li$^+$ is employed to conduct the charges. Free from conducting charges correspondingly, Cu^{2+} and Zn^{2+} cations simply take part in electrode reactions, and thus avoid the cross-over of the cations.

Fig. 2b shows the Nyquist plot of the system. The outline of the plot suggests a fairly typical electrochemical system involving mass-transfer and kinetic control located at low and high frequencies, respectively.[43–45] The inset displays the equivalent circuit, where R$_\Omega$ represents the resistance of the Li$^+$ passing through the Cu^{2+}/Zn^{2+} solutions and of course, the separator.

Fig. 2c outlines the charge-discharge curves at various rates. The electrochemical window is 0.5–1.5 V. There are notable plateaus located at different voltages for charge and discharge processes. The plateau gap reflects the ohmic drop which is mainly raised by the R$_\Omega$ discussed in Fig 2b. Therefore decreasing R$_\Omega$ by optimizing the ion-block membrane would be helpful to enhance the performance of the system. The practical capacity based on the mass of active cathode material of 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. The high capacity for CuSO$_4$ in aqueous solution can be ascribed to the lack of steric hindrance to hold 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 and the rate performance as well (Fig. 2d).

To validate the ECM modeled mechanism, the concentration changes of Cu^{2+} and Li$^+$ in cathode side during a typical charge-discharge process are carried out by an *ex-*

situ ICP-AES approach. The results are presented in Fig. 3. At the beginning of charging, the concentration of Cu^{2+} in the cathode side was low and rose up gradually. Apparently, the increase of the Cu^{2+} concentration indicates the reaction: Cu

5 $\rightarrow Cu^{2+} + 2e^-$. When the system was discharged, the Cu^{2+} concentration turned back to decrease gradually, and recovered itself at the end of discharge. This process is in agreement with the reverse reaction: $Cu^{2+} + 2e^- \rightarrow Cu$. While in the case of Li^+, a converse change occurred. When the

10 amount of Cu^{2+} was increased during charging, Li^+ passed through the membrane from Cu side to Zn side, as a result, the concentration of Li^+ in Cu side was decreased in a mole ratio of 2:1 with Cu^{2+}. When the system was discharged, the concentration of Li^+ in Cu side was recovered. On the whole,

15 the concentration swings of Li^+ and Cu^{2+} are well in agreement with the ECM model.
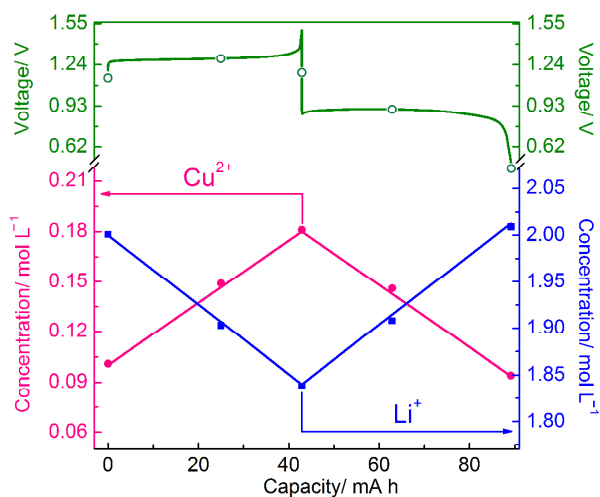
Fig. 3 The concentration changes of Cu^{2+} and Li^+ in cathode side during a typical charge-discharge at a current density of 6

20 mA cm^{-2}.

According to the ECM model, the metallic Cu electrode operates as the current collector of the cathode to receive the electrons coming from the outer circuit when the battery is discharged, and thus the Cu electrode can be replaced by a

25 carbon brush which is more often used as the current collector. We thereby fabricate the Zn| $ZnSO_4$ + Li_2SO_4|ion-block membrane| $CuSO_4$ + Li_2SO_4|carbon (Zn-C) system, where the carbon brush is used as the current collector for cathode. Equally, when the system is charged, the zinc

30 electrode performs as the anode current collector that can thereby be replaced by a piece of stainless steel to collect electrons, and the system composed of stainless-steel| $ZnSO_4$ + Li_2SO_4|ion-block membrane| $CuSO_4$ + Li_2SO_4|Cu (SS-Cu) can be constructed. The Zn-C and SS-Cu systems can both be

35 charged and discharged just like the Zn-Cu system. However, the coulombic efficiencies for the two systems are lower than that of Zn-Cu system (Fig. S6, S7). As a result, the Zn-Cu system looks as if it were the couple of the Zn-C and SS-Cu system. This result is own to that the electron-receive process

40 is always involved with the deposition of Cu^{2+} on the surface of carbon brush or Zn^{2+} on the surface of the stainless steel. During this depositing process, an over potential have to be

surmounted, which would consume extra energies.
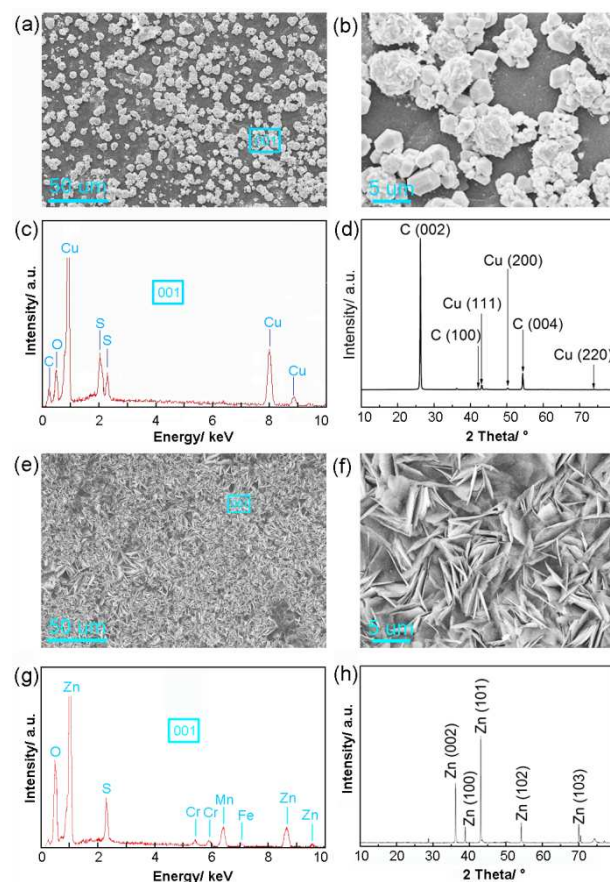
45 **Fig. 4** (a) and (b) The surface and the surface detail of the carbon brush in the Zn-C system after discharging. (c) The EDS results for the selected area in Fig. 4a. (d) The XRD pattern of the carbon brush. (e) and (f) The surface and the surface detail of the stainless steel current collector in the SS-

50 Cu system after charging. (g) The EDS results for the selected area in Fig. 4e, and (h) The XRD pattern of the stainless steel.

Fig. 4 presents the characteristics of these deposits. Fig. 4a shows the surface of the carbon brush covered by copper in the Zn-C system after discharging. It is very clear that

55 particles of the deposits scatter on the carbon brush. Fig. 4b reveals that the deposits are composed of fine crystals accompanied by amorphous phases. The EDS shown in Fig. 4c determines that the selected area in Fig. 4a contains mainly carbon and copper associated with a little O and S which is

60 believed coming from the electrolyte. The XRD result in Fig. 4d confirms the existence of the graphitized carbon and the metallic copper. Fig. 4e gives the morphology of Zn deposits on the surface of the stainless steel in the SS-Cu system after charging. Unlike the scattered copper particles on the carbon

65 brush, flake zinc is dense and compact which is exhibited in Fig. 4e and 4f. Fig. 4g gives the EDS result for the selected area noted as (001) in Fig. 4e. It shows that the surface contains Cr, Mn, Fe, the ingredients of the stainless steel and element Zn, S and O. Among these components, S and O are

70 believed coming from the electrolyte involving oxidation

process since the flake zinc is readily to be oxidized. Fig. 4h demonstrates that the surface is composed of metallic zinc in hexagonal phase. These results agree well with the prediction of the ECM model.

In summary, we propose an electrochemical messenger model to fabricate a rechargeable Zn-Cu Daniell-type battery. In this model, Li^+ operates as a messenger driven by the potential of the battery, to coordinate the behaviors of Cu^{2+} and Zn^{2+}. The ECM modeled Zn-Cu Daniell type battery can offer 0.96 V output voltage at a high current density of 1 mA cm^{-2} with a notable high practical capacity of 330 mA h g^{-1} for $CuSO_4$. In addition, this model might be a feedback to understand the work mechanism of neurotransmitters including Ca^{2+} in human bodies that has come to be viewed as an organic group of electronic circuits.

Notes and references

Jiangsu Key Laboratory of Advanced Catalytic materials and technology, Changzhou University, Changzhou, China. E-mail: jinhongshi0001@163.com

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