A membrane-free Interfacial Battery with High Energy Density

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A membrane-free Interfacial Battery with High Energy Density

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A new concept of membrane-free interfacial battery based on a biphasic system was proposed for the first time. An aqueous $ZnBr_2$ solution was used as negative electrolyte, while Br_2 in CCl_4 served as positive electrolytes. The interfacial Zn/Br_2 battery demonstrated a very impressive performance with a CE of 96% and an EE of 81% at a current density of 15 mA cm^{-2}.

Renewable energies like solar and wind power become more and more important due to the critical issues from energy shortage and high environmental burden from fossil fuels. However, the intermittent and random nature of renewable energies will threaten the stability of the grid. Energy storage device could provide an effective solution to solve these problems and balance the mismatch between supply and demand.[1-4] A flow battery (FB) is regarded as one of the most promising candidates for stationary energy storage,[5-7] due to its prominent merits like independent power and capacity, long cycle life and high safety.[8-14] In principle, different redox couples can create different flow batteries, among which the vanadium and zinc-bromine flow battery [15-21]are currently at the demonstration stage. Quite recently, some new flow battery systems like quinone/bromine, hydrogen/bromine, quinone/iron have been developed to improve the energy density and decrease the cost and further create a more economic stationary storage system.[22-25] For traditional flow batteries, an ion-selective membrane is indispensable to prevent the crossover of active species, while transport ions to form the internal circuit. However, the low selectivity of a membrane normally induces irreversible capacity decay and further shortens the cycle life of a battery. Especially for bromine based flow batteries, the crossover of highly corrosive Br_2 seriously affects the battery cycle life and brings environmental problems. In addition, considering the critical medium of a battery (strongly acidic or alkaline conditions, highly oxidative) a membrane will definitely lead to a cost issue of a stack.

Up to now, the way to eliminate membrane in flow batteries is developing microfluidic batteries, which create laminar flow of electrolytes under specific condition based on the hydrodynamic engineering. However, these batteries can only work at microscale and are not easy for scale-up.[22] Recently, Marcilla proposed a membrane-free redox battery, however, the ion transport rate through organic phase is rather slow, leading to super low power density.[26] (The current density is around 0.2 mA/cm^2)

Here, for the first time, we propose and demonstrate an evolutional membrane–free interfacial battery at macro-scale. Two immiscible phases, which can dissolve positive and negative redox couples respectively, were employed to internally avoid electrolytes contamination. The electrochemical reaction occurs only at the interface of the two phases, from which we derived the name interfacial battery. In this design, the very thin interface between two phases can certainly shorten the ion transport path between anode and cathode and further ensure the higher power density. The proof-of-concept is demonstrated by using Zinc/Bromine as redox couples. In the design, $ZnBr_2$ aqueous solution served as negative electrolyte, while, positive electrolyte is the Br^-/Br_2 in CCl_4. (Figure 1) During charging process, the Zn^{2+} is reduced to zinc metal and the Br^- is oxidized to free bromine at the interface, which will be immediately dissolved in CCl_4. During discharge, the zinc metal will be oxidized to Zn^{2+} and the Br_2 will be reduced to Br^- at the interface during discharge process. Compare with the traditional zinc bromine flow battery, the interfacial ZBFB battery can effectively prevent the cross mix of Br_2 due to the dramatical difference of its solubility in CCl_4 and water, thus eliminating the need for a membrane. Moreover, compared with traditional zinc bromine flow battery, a interfacial battery avoids the employment of the pumps and a membrane, therefore, it achieves a great advantages in terms of cost. The electrochemical properties of proposed interfacial battery were investigated in detail.

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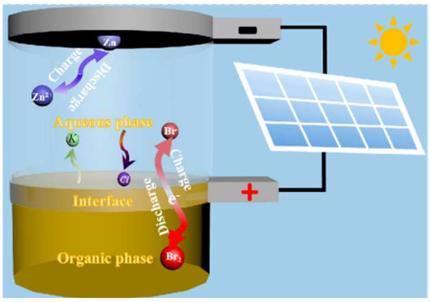

Figure 1. The schematic diagram of the interfacial battery

The electrochemical activity of Br^-/Br_2 and Zn/Zn^{2+} on graphite in CCl_4 and water was investigated by CV. As shown in Figure 2A, no obvious oxidization or reduction peaks were observed in CV curves, when pure CCl_4 or CCl_4 with 0.1M Br_2 were employed as the electrolyte, indicating that the graphite electrode showed no electrochemical activity on Br_2 in CCl_4, in another word, the electrochemical reaction at the positive side can only occur at the interface between water and CCl_4. The bromine reduction peak under aqueous phase or at the interface was carried out on the electrolyte with the composition of 2 M $ZnBr_2$+3 M KCl+0.4 M 1-methyl-1-ethylpyrrolidinium bromide (MEP). The peak current for the oxidization reaction was not observed because of the high concentration of bromine ions, which indicates that the reaction rate is not limited by mass-transfer. The electrochemical properties of Br^-/Br_2 couples on graphite electrode at different scan rates were detected as well (Figure S1, Supporting information). The reduction peak current changed slightly with the increase of the scan rate, which indicates that the reduction reaction of Br^-/Br_2 on graphite is mainly controlled by the electrochemical reaction step.

Similarly with traditional zinc bromine flow battery, the electrochemical behaviour of Zn/Zn^{2+} at negative side is the deposition and dissolution of zinc metal (Figure 2B). The reduction current for the Zn^{2+} started at approximately at -1.02 V versus SCE, and the stripping current occurred in the region of -0.95 V to -0.75 V.

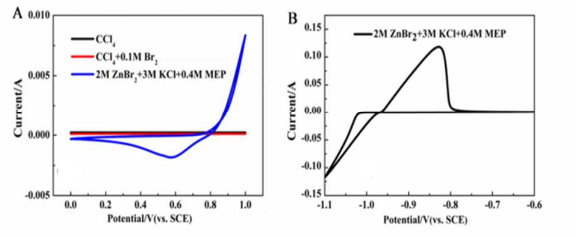

Figure 2. The CV curves of Br^-/Br_2 (A) and Zn/Zn^{2+} (B) on graphite performed in various electrolytes at a scan rate of 10 mV/s

The validity of interfacial battery is confirmed by a single cell test, the detailed structure of the cell was demonstrated in supporting information (Figure S3). The visual pictures of the cell at discharge state and charge state are shown in supporting information (Figure S2). The charge-discharge tests were carried out at constant current densities ranging from 5 to 15 mA cm^{-2}, a $ZnBr_2$ concentration of 2 M was used. The typical charge-discharge curves of a cell at current densities of 5 mA cm^{-2}, 10 mA cm^{-2}, 15 mA cm^{-2} are presented in Figure 3A. The cell maintained good charge-discharge performance at different current densities. It showed higher charge voltage and lower discharge voltage between the charge and discharge processes at a higher current density, which is due to the higher polarization. As shown in Figure 3B, the VE of the battery decreases from 91% to 84% when the current density increases from 5 mA cm^{-2} to 15 mA cm^{-2}, while the CE increases from 94% to 96%. As a result, the EE of the interfacial battery reaches the highest value of 86% at a current density of 5 mA cm^{-2}. And EE decreases from 85% to 81%, when the current density increases to 10 mA cm^{-2} and 15mA cm^{-2}, respectively. This performance is comparable with the traditional zinc bromine flow batteries.[19] Compare the reported biphasic flow batteries, the interfacial battery possessed a much shorter ion transport distance and a much higher power density or can operate at a much higher current density ,[26]further confirming our idea.

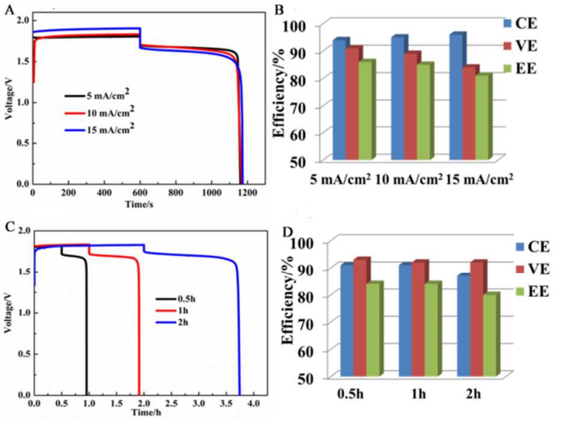

Figure 3. The charge-discharge curves and efficiency of an interfacial battery at various current densities (A, B) and different charge time (C, D) at a current density of 5 mA/cm^2.

Voltage profiles of the battery, which were charged for different times at a current density of 5 mA cm^{-2}, are shown in Figure 3C. As the charge time increased from 0.5 h to 1 h, there is little change in the CE, which stays at around 91%. This may be attributed to the higher self-discharge related to the diffusion of bromine to the anode. The decrease in the CE with the increasing charge time could lead to a drop in EE. The EE of the battery decreases from 84% to 80% (Figure 3D), when the charge time increases from 0.5 h to 2 h.

To further confirm the availability of this battery, a LED was successfully lighted up, when the positive electrode is at interface. Then the positive electrode was gradually moved from interface to CCl_4 phase and the LED was turned off, when the electrode reached the CCl_4 phase (Figure 4B), which well confirmed that the electrochemical reaction occurred at the interface (see the video in supporting information).

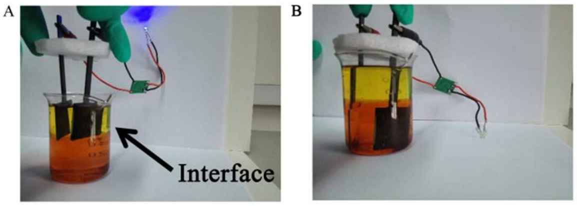

Figure 4. The situation of the LED when the electrode at the interface (A) and under the interface or in the CCl_4(B)

The energy density is a critical parameter for a battery in practical applications. In this design, the high solubility of $ZnBr_2$ in water and high solubility of Br_2 in CCl_4 could create a high theoretical energy density of 495.8Wh/L. To improve the energy density of proposed interfacial battery, the concentration of $ZnBr_2$ was increased from 2M to 5M. The performance of the batteries with 3M and 5M $ZnBr_2$ at different current densities is shown in Figure S4 (Supporting Information). It can be seen that the VE drops a little with the increase of the $ZnBr_2$ concentration at the same current density, which may be due to the decreased ion conductivity of electrolytes (Figure S5, Supporting Information). Even with the concentration as high as 5 M, the cell exhibited an energy efficiency of 80% at a current density of 5 mA cm^{-2}, showing very promising performance. With 5 M $ZnBr_2$, an energy density of 62.6Wh/L can be obtained (Figure S6), which is very competitive compared with other flow battery systems (Figure 6).

The self-discharge of a cell was detected after charge-discharge tests. Figure S7 shows the voltage profiles of a battery as a function of time during the self-discharge, after charging it for 10 min at 15 mA cm^{-2}. The open-circuit cell voltage shows no obvious decay in 12 hours, showing a low self-discharge rate.

The long-term cycling performance of the proposed interfacial battery was investigated by extended charge-discharge tests at 5 mA cm^{-2} (Figure 5). The battery kept a very stable performance after continuously running form more than 200 cycles, which implies very good stability. Further improvement in the battery performance can be realized by cell design and the composition of the electrolyte.

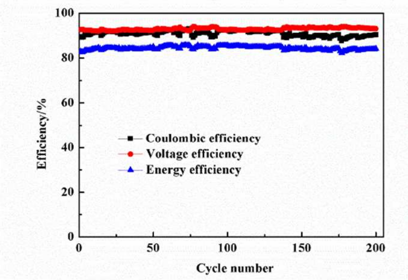

Figure 5. The charge-discharge cycling performance of the interfacial battery at 5mA cm^{-2}

Combing the low cost, high energy density, simple structure and the good performance, the interfacial battery exhibits a great advantage in terms of capital cost. Based on the electrolyte cost and the other components cost, the cost of Zn/Br_2 interfacial battery is around 71.7$/kWh (Table S1-S5), which is much lower than that of the most reported flow battery systems (Figure 6).[27-30]

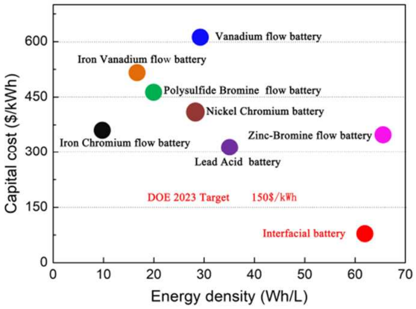

Figure 6. The capital cost of different kinds of battery.

In summary, we proposed for the first time, a membrane-free interfacial battery concept and demonstrated its feasibility by constructing a Zn/Br_2 interfacial battery. The battery could internally solve the crossover problems of redox couples. The battery delivers a very impressive charge and discharge performance with an EE of 81% at a current density of 15 mA/cm2 as well as excellent cycle stability. The advantages of low cost, simple design and high energy density make the interfacial battery a very promising candidate for stationary energy storage.

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Conflicts of interest

There are no conflicts to declare.

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A new concept of membrane-free interfacial battery was designed and presented.