

Energetic Zinc Ion Chemistry: The Rechargeable Zinc Ion Battery**

Chengjun Xu, Baohua Li, Hongda Du, and Feiyu Kang*

Energy-storage devices are now powering our world. An ideal energy-storage device that is characterized by high capacity, fast charge/discharge capability, safety, environmental friendliness, and low cost is of vital importance for today's society. Our society has been seeking such ideal devices for various applications such as consumer electronics, electric vehicles, transportation, and military demands. However, existing aqueous energetic batteries or power-type supercapacitors are far from achieving the final goals. Herein we report a unique zinc ion battery chemistry for the preparation of a new safe and environmentally friendly zinc ion battery. The zinc ion battery can deliver a high capacity and can be charged or discharged within 30 seconds.

Batteries such as alkaline Zn/MnO₂, lithium ion, metal hydride (Ni–MH), lead–acid (Pb acid), and nickel–cadmium (Ni–Cd) batteries are widely used. For example, since their invention in 1860, alkaline Zn/MnO₂ batteries have become dominant in primary battery chemistry with an annual 10 billion dollars market.^[1–3] It is well known that energetic batteries generally provide limited power, whereas supercapacitors provide low energy. A few lithium ion batteries may deliver both high power and energy density, but the safety and environmental issues cannot be ignored.^[5,6] New battery chemistry and architecture are required for rechargeable batteries with high capacity and fast charge/discharge capability as well as safety and ecofriendliness.

Herein, we present a safe and ecofriendly power-type battery, which composes of an α -MnO₂ cathode, a zinc anode, and a mild ZnSO₄ or Zn(NO₃)₂ aqueous electrolyte (Figure 1). The construction of this new battery is based on the following two electrochemical processes [see Eqs. (1) and (2)]. First, in a mild aqueous solution containing Zn²⁺ ions, zinc can rapidly electrochemically dissolve as Zn²⁺ ion and deposit reversibly, which delivers a very high capacity of 820 mAhg^{−1}.^[3,4] Second, we found that Zn²⁺ ions can be reversibly intercalated into tunnels of α -MnO₂ in the same mild system, which ultimately results in a large capacity of 210 mAhg^{−1}.^[5] These two processes both involve the partic-

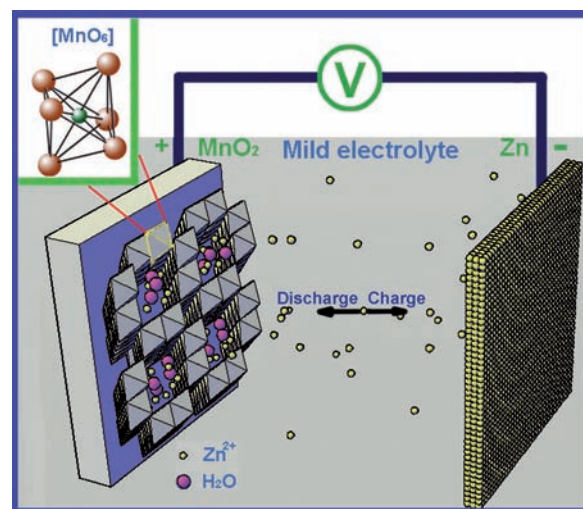


Figure 1. Schematics of the chemistry of the zinc ion battery. Zn²⁺ ions migrate between tunnels of an α -MnO₂ cathode and a Zn anode. The inset in the upper left corner shows the structural basic unit of the MnO₆ octahedron of MnO₂.

ipation of Zn²⁺ ions in a mild electrolyte. Therefore, we use Zn²⁺ ions as a medium to connect MnO₂ with zinc to produce a new rechargeable battery. The battery chemistry is shown in Figure 1. During discharging, anodic zinc is dissolved in the form of Zn²⁺ ions, which rapidly diffuse and intercalate into an α -MnO₂ cathode to generate an electron current flow in the electrical loop. Since the charge storage mechanism is based on the migration of Zn²⁺ ions between cathode and anode, we refer to it as a zinc ion battery (ZIB).

Compared with lead, lithium, magnesium, or cadmium, zinc is a nontoxic, abundant, and low-cost resource. In a mild ZnSO₄ or Zn(NO₃)₂ aqueous solution containing Zn²⁺ ions, the electrochemical dissolution and deposition process of zinc can occur above and below 0 V vs. Zn²⁺/Zn as shown in Figure 2 (red line).^[7–12] Because of its relatively low potential, this rapid and reversible process is ideal as the anodic reaction [Eq. (1)].



In contrast, the structural frameworks of α -MnO₂ consist of large and stable tunnels, which can be filled with foreign cations, such as Zn²⁺ ion. Recently, we proposed a multivalent cation charge-storage mechanism of MnO₂ and found that Zn²⁺ ions can be stored in tunnels of α -MnO₂ in a mild Zn(NO₃)₂ electrolyte.^[13–20] The intercalation of zinc ions into cathodic crystalline α -MnO₂ can be characterized by electrochemical tests or by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) measurements. As shown in

[*] Dr. C. Xu, B. Li, H. Du, Prof. F. Kang
Advanced Materials Institute, Graduate School at
Shenzhen Tsinghua University (China)

Prof. F. Kang
Laboratory of Advanced Materials, Department of
Materials Science and Engineering, Tsinghua University (China)
E-mail: fykang@tsinghua.edu.cn

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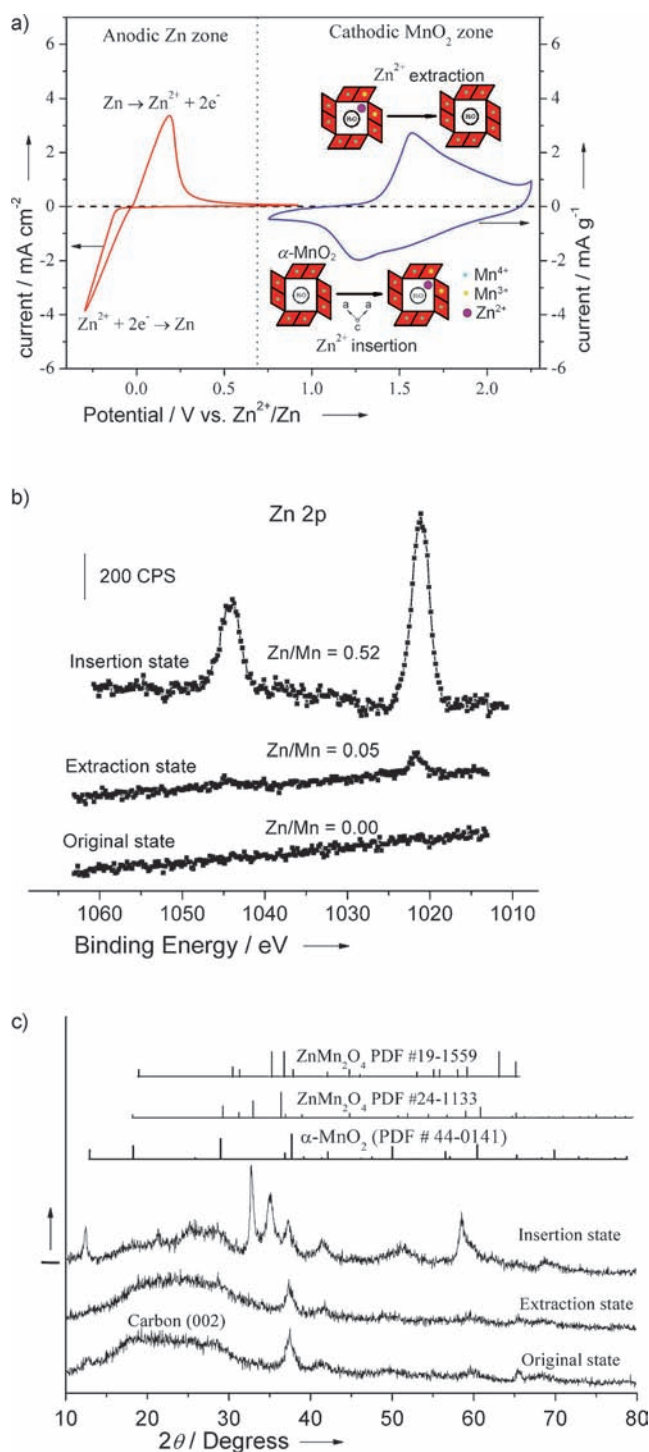
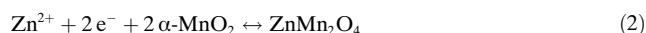


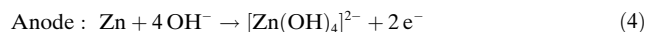
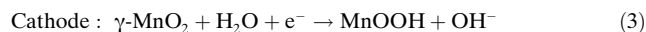
Figure 2. a) Cyclic voltammogram of the zinc anode (red line) and the α -MnO₂ cathode (blue line) at 2 mV s⁻¹ in 0.1 mol L⁻¹ Zn(NO₃)₂ aqueous electrolyte (pH 5.2). The plot shows the anodic and the cathodic processes of the zinc ion battery, respectively. b) Zn 2p core level spectra of cathodic crystalline α -MnO₂ electrodes in the original, extraction, and insertion states. c) XRD patterns of cathodic crystalline α -MnO₂ electrodes in the original, extraction, and insertion states.

Figure 2a (blue line) there are two distinguishable peaks at around 1.3 V and 1.7 V vs. Zn²⁺/Zn during cycling. We performed XPS and XRD analysis on cathodic crystalline

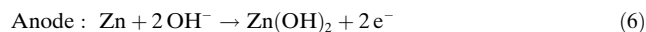
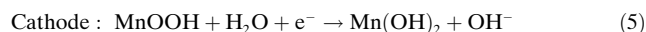
electrodes in original, extraction (potentiostated at 1.7 V), and insertion (potentiostated at 1.3 V) states. Zn 2p core level spectra of α -MnO₂ electrodes in original, extraction, and insertion states are shown in Figure 2b. The augment of intensity of Zn 2p from extraction to insertion states clearly confirms the insertion/extraction of Zn²⁺ ion into/from α -MnO₂. XRD patterns of α -MnO₂ electrodes in original, extraction, and insertion states are shown in Figure 2c. In the insertion state, the formation of ZnMn₂O₄ clearly confirms the insertion of Zn²⁺ ion into α -MnO₂, while in the extraction state there is just α -MnO₂. Therefore, the two distinguishable peaks at around 1.3 and 1.7 V peaks were confirmed to be storage/release of Zn²⁺ ions into/out of crystalline α -MnO₂ tunnels. This cathodic process can be described by Equation (2).



Based on the unique zinc ion chemistry [Eqs. (1) and (2)], we assembled the integral and practical prototype ZIBs (see the Experimental Section). It should be noticed that the structure of the ZIB is very close to that of the widely used alkaline Zn/MnO₂ battery, which normally uses γ -MnO₂ or δ -MnO₂ as the cathode and the alkaline solutions (KOH or NaOH) as the electrolyte. However, their battery chemistries are quite different. The battery chemistry of the ZIB is based on Equation (1) as the anode reaction and Equation (2) as the cathode reaction. Against that, the so-called two-step (two-electron) pathways governs the battery chemistry in Zn/MnO₂ batteries.^[1,7,8] The first electron discharge of the alkaline Zn/MnO₂ cell could be expressed by Equations (3) and (4).



If the cell continues to discharge, the cathode and anode of the alkaline Zn/MnO₂ battery are further irreversibly reduced in a second step [Eqs. (5)–(7)].



The open circuit voltage (OCV) of the ZIB is approximately 1.5 V, which is close to that of primary Zn/MnO₂ batteries.^[1,7,8] Figure 3a shows the discharge capacity of the ZIB at various rates. A rate of n C corresponds to a full discharge in $1/n$ h. At 0.5 C, the ZIB delivers a high capacity of 210 mAh g⁻¹, which is higher than that of primary alkaline Zn/MnO₂ batteries (125 mAh g⁻¹).^[21,22] At 126 C within 27 s it delivers a relatively high capacity of 68 mAh g⁻¹. The continuous charge–discharge curves can be seen in Figures S125 and S126 in the Supporting Information. The cycle life performance of the ZIB in terms of capacity retention and coulombic efficiency was also investigated by a continuous cycling test at 6 C charge/discharge rate. As shown in Fig-

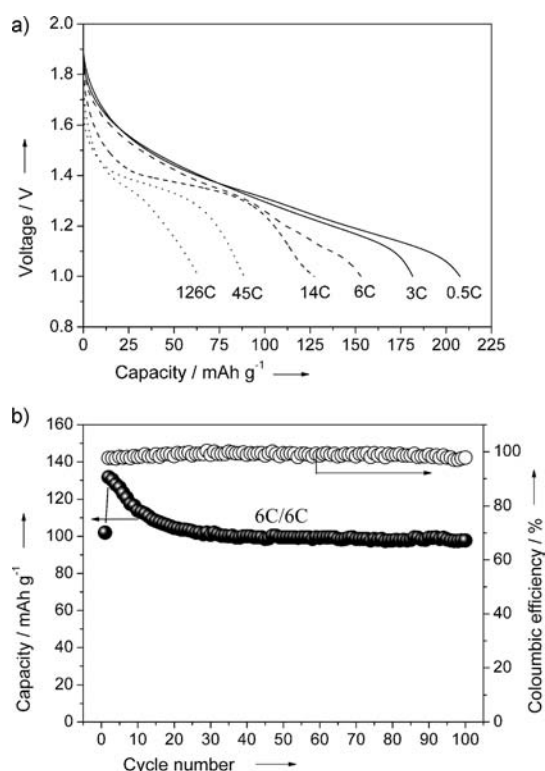


Figure 3. a) Discharge curves of the ZIB at various rates. A rate of nC corresponds to a full discharge in $1/n$ h. b) Cycle life performance of the ZIB at a continuous cycling 6C/6C charge/discharge test.

ure 3b, after 100 cycles, the discharge capacity of the ZIB still remains near 100% of original values and the coulombic efficiency is about 100% for all cycles, indicating a high utility of electric capability. The ZIB is characterized by an excellent rechargeability in terms of capacity retention and coulombic efficiency even at 100% depth of discharge, whereas it is well known that Zn/MnO₂ batteries are normally primary or can be cycled only a limited number of times.^[1,3,4,9]

The most interesting point of the ZIB is the use of a nontoxic, noncorrosive, and low cost mild aqueous electrolyte, such as aqueous solutions of ZnSO₄ or Zn(NO₃)₂. It is well known that state-of-the-art aqueous rechargeable batteries use one of two kinds of corrosive electrolytes, either alkaline (such as Zn/MnO₂, Ni–Cd, or Ni–MH batteries), or acid (lead–acid).^[1,2] In addition, the components of the ZIB, such as MnO₂, Zn, and the mild electrolytes, are all low cost, nontoxic, and abundant in raw materials. Furthermore, we have performed the nailing experiment on a soft-packed ZIB at a fully charged state. No sign of flash or smoke has been detected, which indicates the excellent safety of the ZIB. These particularities label the ZIB as a low cost, safe, and environmentally friendly power source. This is the first step in the production of the ZIB. With good engineering, ZIBs can be environmentally friendly, reliable, safe, and low-cost power sources applied in occasions in which both high energy and power densities are necessary.

Experimental Section

We assembled standard and practical coin cells and soft-packed cells to characterize the electrochemical performance of zinc ion batteries. Detailed information about the synthesis process of MnO₂ and assembly of batteries are given in the Supporting Information. The galvanostatic charge/discharge cycling tests of ZIBs were performed in a voltage window ranging from 1.0 to 1.9 V. The discharge capacity of the cell was calculated according to Equation (8) for the third cycle, where C is the specific capacity (mAh g^{−1}), I is the applied current (mA), t is discharge time (h), and m is the mass of the active material (g).

$$C = It/m \quad (8)$$

The coulombic efficiency is given by the discharge time/charge time ratio.

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