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

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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 important 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/MnO_2, 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/MnO_2 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-MnO_2 cathode, a zinc anode, and a mild $ZnSO_4$ or $Zn(NO_3)_2$ 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 Zn^{2+} ions, zinc can rapidly electrochemically dissolve as Zn^{2+} ion and deposit reversibly, which delivers a very high capacity of 820 mAh g^{-1}.[3,4] Second, we found that Zn^{2+} ions can be reversibly intercalated into tunnels of α-MnO_2 in the same mild system, which ultimately results in a large capacity of 210 mAh g^{-1}.[5] These two processes both involve the participation of Zn^{2+} ions in a mild electrolyte. Therefore, we use Zn^{2+} ions as a medium to connect MnO_2 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 Zn^{2+} ions, which rapidly diffuse and intercalate into an α-MnO_2 cathode to generate an electron current flow in the electrical loop. Since the charge storage mechanism is based on the migration of Zn^{2+} ions between cathode and anode, we refer to it as a zinc ion battery (ZIB).

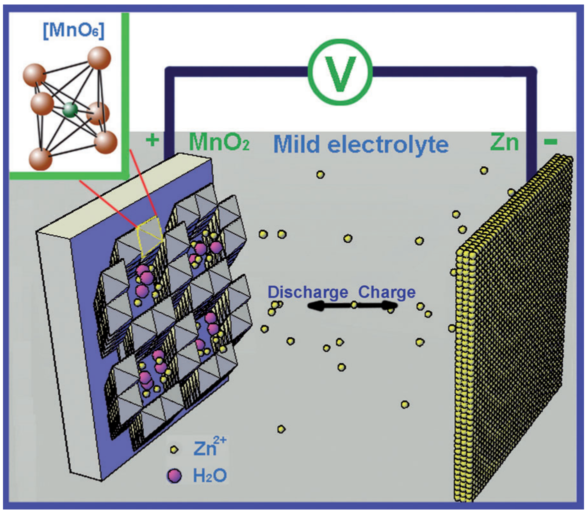

Figure 1. Schematics of the chemistry of the zinc ion battery. Zn^{2+} ions migrate between tunnels of an α-MnO_2 cathode and a Zn anode. The inset in the upper left corner shows the structural basic unit of the MnO_6 octahedron of MnO_2.

Compared with lead, lithium, magnesium, or cadmium, zinc is a nontoxic, abundant, and low-cost resource. In a mild $ZnSO_4$ or $Zn(NO_3)_2$ aqueous solution containing Zn^{2+} ions, the electrochemical dissolution and deposition process of zinc can occur above and below 0 V vs. Zn^{2+}/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)].

$$Zn \leftrightarrow Zn^{2+} + 2\,e^- \tag{1}$$

In contrast, the structural frameworks of α-MnO_2 consist of large and stable tunnels, which can be filled with foreign cations, such as Zn^{2+} ion. Recently, we proposed a multivalent cation charge-storage mechanism of MnO_2 and found that Zn^{2+} ions can be stored in tunnels of α-MnO_2 in a mild $Zn(NO_3)_2$ electrolyte.[13–20] The intercalation of zinc ions into cathodic crystalline α-MnO_2 can be characterized by electrochemical tests or by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) measurements. As shown in

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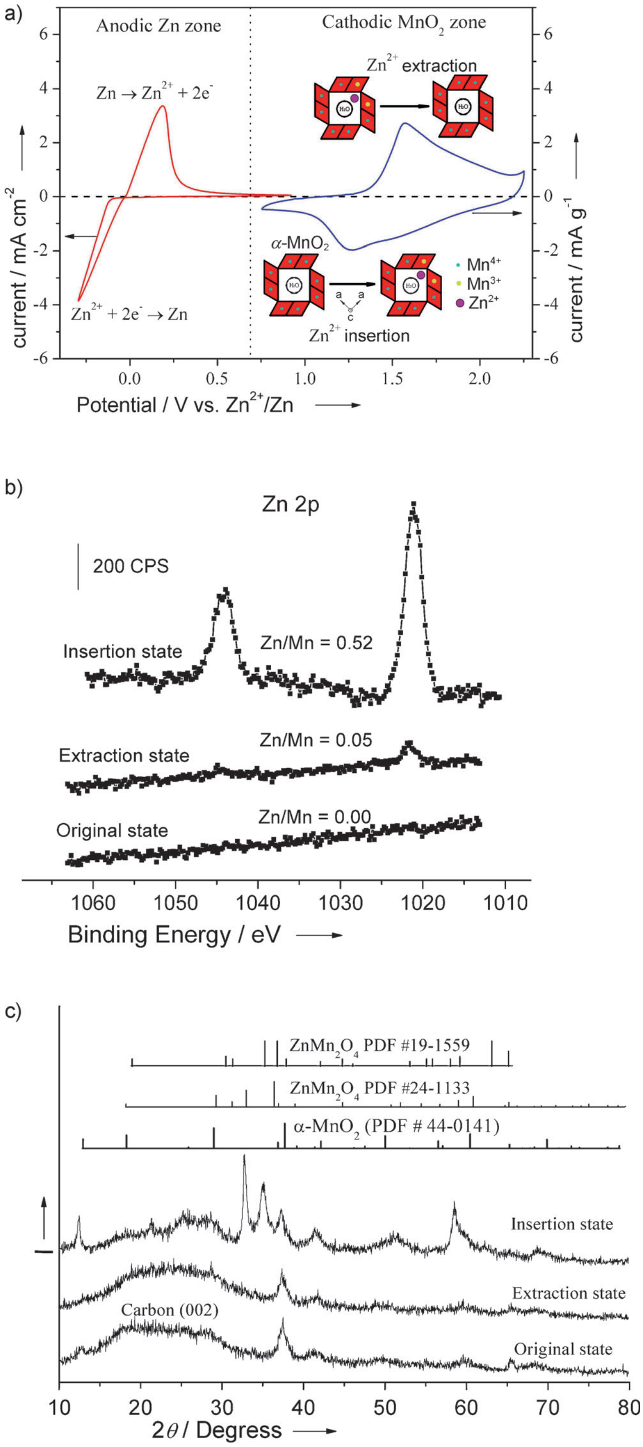

Figure 2. a) Cyclic voltammogram of the zinc anode (red line) and the α-MnO_2 cathode (blue line) at $2\ mV\,s^{-1}$ in $0.1\ mol\,L^{-1}$ $Zn(NO_3)_2$ aqueous electrolyte (pH 5.2). The plot shows the anodic and the cathodic processes of the zinc ion battery, respectively. b) Zn 2p core level spectra of cathodic crystalline α-MnO_2 electrodes in the original, extraction, and insertion states. c) XRD patterns of cathodic crystalline α-MnO_2 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. Zn^{2+}/Zn during cycling. We performed XPS and XRD analysis on cathodic MnO_2 electrodes in original, extraction (potentiostated at 1.7 V), and insertion (potentiostated at 1.3 V) states. Zn 2p core level spectra of α-MnO_2 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 Zn^{2+} ion into/from α-MnO_2. XRD patterns of α-MnO_2 electrodes in original, extraction, and insertion states are shown in Figure 2c. In the insertion state, the formation of $ZnMn_2O_4$ clearly confirms the insertion of Zn^{2+} ion into α-MnO_2, while in the extraction state there is just α-MnO_2. Therefore, the two distinguishable peaks at around 1.3 and 1.7 V were confirmed to be storage/release of Zn^{2+} ions into/out of crystalline α-MnO_2 tunnels. This cathodic process can be described by Equation (2).

$$Zn^{2+} + 2\,e^- + 2\,\alpha\text{-}MnO_2 \leftrightarrow ZnMn_2O_4 \qquad (2)$$

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/MnO_2 battery, which normally uses γ-MnO_2 or δ-MnO_2 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/MnO_2 batteries.[1,7,8] The first electron discharge of the alkaline Zn/MnO_2 cell could be expressed by Equations (3) and (4) .

$$\text{Cathode}: \ \gamma\text{-}MnO_2 + H_2O + e^- \rightarrow MnOOH + OH^- \qquad (3)$$

$$\text{Anode}: \ Zn + 4\,OH^- \rightarrow [Zn(OH)_4]^{2-} + 2\,e^- \qquad (4)$$

If the cell continues to discharge, the cathode and anode of the alkaline Zn/MnO_2 battery are further irreversibly reduced in a second step [Eqs. (5)–(7)].

$$\text{Cathode}: \ MnOOH + H_2O + e^- \rightarrow Mn(OH)_2 + OH^- \qquad (5)$$

$$\text{Anode}: \ Zn + 2\,OH^- \rightarrow Zn(OH)_2 + 2\,e^- \qquad (6)$$

$$\text{or } Zn(OH)_2 \rightarrow ZnO + H_2O \qquad (7)$$

The open circuit voltage (OCV) of the ZIB is approximately 1.5 V, which is close to that of primary Zn/MnO_2 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/MnO_2 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 SI25 and SI26 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-

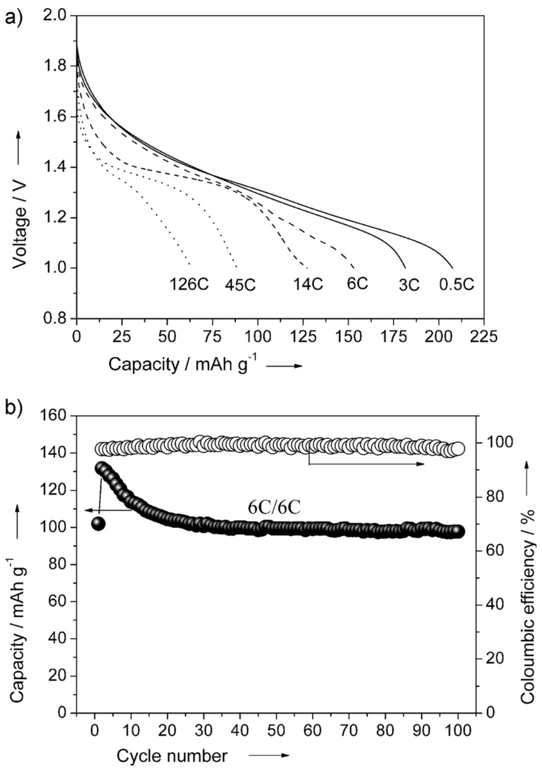

Figure 3. a) Discharge curves of the ZIB at various rates. A rate of *n*C corresponds to a full discharge in 1/*n* h. b) Cycle life performance of the ZIB at a continuous cycling 6C/6C charge/discharge test.

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/MnO_2 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 $ZnSO_4$ or $Zn(NO_3)_2$. 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/MnO_2, Ni–Cd, or Ni–MH batteries), or acid (lead–acid).[1,2] In addition, the components of the ZIB, such as MnO_2, 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 MnO_2 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).

$$C = I\,t/m \tag{8}$$

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

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