Supporting Information

**High-performance Zn battery with transition metal ions co-regulated electrolytic MnO2**

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Experimental

**Chemicals:** Manganese sulfate monohydrate (MnSO4·H2O, ≥ 99.0%), nickel(II) sulfate hexahydrate (NiSO4·6H2O, ≥ 99.5%), cobalt(II) sulfate heptahydrate (CoSO4·7H2O, ≥ 99.5%), zinc sulfate heptahydrate (ZnSO4·7H2O, ≥ 99.5%) and sulfuric acid (H2SO4, 95.0-98.0 %) were purchased from Sinopharm Chemical Reagent Co., Ltd. All raw materials purchased in this work were of analytical grade and used without further purification. The ultra-pure water (electrical resistivity: 18.2 MΩ·cm) used in this experiment was provided by a laboratory water purification system purchased from Shanghai Hitech Instruments Co., Ltd.

**Electrochemical deposition of Co-Ni-MnO2:** The carbon felt (CF, thickness of 3 mm) used in this work was purchased from Dalian Longtian Tech. Co., Ltd. These CFs with 3D structures could supply effective electrolyte accessible channels for the deposition and stripping of MnO2. Firstly, the pristine CF was placed in a muffle furnace and calcinated in air at 450°C for 2 hours with a heating rate of 4°C/min. The pristine CF was pretreated before use to enhance its hydrophilicity. The heat-treated CF (20 mm × 10 mm × 3 mm) was used as the current-collector for the cathode. A mixed solution consists of 1 M MnSO4·H2O, 0.09 M CoSO4·7H2O, 0.06 M NiSO4·6H2O and 0.1 M H2SO4 was used as the electrolyte. The Co-Ni-MnO2 cathode was obtained by an electrochemical deposition method with a constant potential of 1.13 V vs Ag/AgCl to a capacity of 10 mAh cm-2 in a three-electrodes system. Similarly, the Co-MnO2, Ni-MnO2 and MnO2 cathodes were obtained by the same electrochemical deposition method in the electrolytes without NiSO4·6H2O and/or CoSO4·7H2O.

**First-principles calculations:** The First-principles calculations were carried out by using Vienna Ab-initio Simulation Package (VASP) software with density functional theory (DFT) and projector augmented-wave plane-wave (PAW) pseudopotential method. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) function was applied to describe the electron exchange-correlation functions. The four crystal surface models, based on shearing the primitive cell of MnO2 along the (211) crystal plane, had a vacuum thickness of 15 Å in the z-direction to avoid interaction between the slabs. The kinetic energy cutoff of electron wave functions was used as 500 eV. The K-point meshes used for the first Brillouin zone integration were generated by Monkhorst-Pack scheme as 3 × 3 × 3. The energy band structure of each system was calculated by the closed K-point grid path of G-F-Q-Z-G. The convergence criterion for the structural optimizations was set as EDIFF = 10-4 and EDIFFG = 10-4. The visualization for electronic and structural analysis (VESTA) software was used to draw the crystal structure diagrams.

**Materials characterization:** X-ray diffraction (XRD) patterns were obtained by a Philips X’Pert PRO SUPER X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.54056 Å). The morphologies and structures of the as-prepared products were characterized by using a scanning electron microscope (SEM, JEOL-6700F). A transmission electron microscope (TEM; JEOL JEM-2100F) at an accelerating voltage of 200 kV, was used to obtain the scanning-transmission electron microscopy (STEM), selected-area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM) images. Surface chemical analysis was performed using an X-ray photoelectron spectrometer (XPS, ESCALAB MK II). The photoluminescence spectra were acquired using a FluoroMax-4 fluorescence spectrophotometer (Horiba Scientific) equipped with a 450 W xenon arc lamp. Ultraviolet-visible (UV-vis) absorption spectra were collected on a Shimadzu UV-3600 spectrophotometer with the spectral region of 200-800 nm. [Fourier](file:///D:\Dict\7.2.0.0703\resultui\dict\?keyword=Fourier) [transform](file:///D:\Dict\7.2.0.0703\resultui\dict\?keyword=transform) [infrared](file:///D:\Dict\7.2.0.0703\resultui\dict\?keyword=infrared) [spectroscopy](file:///D:\Dict\7.2.0.0703\resultui\dict\?keyword=spectroscopy) (FTIR) was recorded by a Nicolet Impact 410 FTIR Infrared Instrument using the KBr pellet technique.

**Electrochemical measurements:** The MnO2 cathode half-cell performances were evaluated by a LAND battery tester (CT2001A, Wuhan, China) in the three-electrode setup at room temperature. A piece of treated carbon-felt (1 mm × 2 cm), a platinum foil and an Ag/AgCl electrode were used as the working, counter and reference electrodes, respectively. All the electrodes were immersed in the electrolyte of MnSO4 and H2SO4 with/without NiSO~~4~~/CoSO4 solution. The carbon felt was half-immersed in the electrolyte with an actual immersion area of 1 cm2. The cell was charged at 1.13 V (vs. Ag/AgCl) to 10 (or 1/3/5) mAh cm-2 with a constant-voltage technique to form the MnO2 layer. The MnO2-Zn full cell was fabricated by using carbon felt as the cathode current collector and Zn foil as the anode. The MnO2-Zn full cell was charged by a constant-voltage technique at 2.2 V, which effectively prevented water splitting while maintaining the depositions of MnO2 and Zn simultaneously. The charging areal capacities varied from 1 mAh cm-2 to 10 mAh cm-2 and then discharged at constant current densities (1/3/5/10/30/50/70/100 mA cm-2) to 0 V. All the electrochemical impedance spectra (EIS) were collected in a Bio-Logic VMP-3 electrochemical workstation by applying an AC voltage with 10 mV of amplitude in a frequency range from 200 KHz to 1 Hz.



**Fig. S1.** (a-d) Four structural models for the first-principles calculations: (a) MnO2, (b) Co-MnO2, (c) Ni-MnO2, (d) Co-Ni-MnO2.



**Fig. S2.** TheCo-Ni-MnO2 structural models of different occupation positions of Co and Ni atoms: (a) Co-Ni-MnO2 (1-2), (b) Co-Ni-MnO2 (1-3), (c) Co-Ni-MnO2 (2-3).

**Table S1.** The minimum formation energy for three different Co-Ni-MnO2 structural models.

|  |  |  |  |
| --- | --- | --- | --- |
| Structure | Co-Ni-MnO2 (1-2) | Co-Ni-MnO2 (1-3) | Co-Ni-MnO2 (2-3) |
| Formation energy | -0.73 | 1.87 | 3.26 |

The structural models of different occupation positions of Co and Ni atoms were optimized and calculated their minimum formation energy. The formula for the formation energy of the Co-Ni-MnO2 structure is defined as follows:

(1)

Here, is the formation energy of the Co-Ni-MnO2 structure. is the [total](file:///D:\Dict\7.2.0.0703\resultui\dict\?keyword=total) [energy](file:///D:\Dict\7.2.0.0703\resultui\dict\?keyword=energy) of the Co-Ni-MnO2 structure. is the total energy of the ideal system (MnO2 structure). is the number of types of all defective chemical elements. is the number of Mn type atoms that are added () or removed () when a defect is formed. is the chemical potential of the Mn type atom. For the α-phase MnO2 system, the chemical potential of Mn and O, referred to as and , must meet the following growth condition:

(2)

Where represents the chemical potential of the α-phase MnO2 system. We calculate the minimum formation energy of the Co-Ni-MnO2 (1-2), Co-Ni-MnO2 (1-3) and Co-Ni-MnO2 (2-3) structures as -0.73 eV, 1.87 eV and 3.26 eV, respectively, according to formulas (1) and (2). The minimum formation energy for three different Co-Ni-MnO2 structure models is provided in Table S1. Obviously, the formation energy of the Co-Ni-MnO2 (1-2) structure is lower than that of Co-Ni-MnO2 (1-3) and Co-Ni-MnO2 (2-3) structures, which indicates that the Co-Ni-MnO2 (1-2) structure is more stable than the Co-Ni-MnO2 (1-3) and Co-Ni-MnO2 (2-3) structures. It may be easier to synthesize the Co-Ni-MnO2 (1-2) structure in experimental conditions. Thus, the Co-Ni-MnO2 (1-2) structure is considered the most reasonable structure for theoretical calculation in this work.

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**Fig. S3.** Band structures of the four theoretical calculation structural models.



**Fig. S4.** (a) Charge-discharge curves and (b) Coulombic, voltage and energy efficiencies of the Co-MnO2 cathode in electrolytes of MnSO4 with different concentrations of CoSO4 to a capacity of 10 mAh cm-2.



**Fig. S5.** (a) Charge-discharge curves and (b) Coulombic, voltage and energy efficiencies of the Ni-MnO2 cathode in electrolytes of MnSO4 with different concentrations of NiSO4 to a capacity of 10 mAh cm-2.



**Fig. S6.** Charge-discharge curves of the MnO2 and Co-Ni-MnO2 cathodes in electrolytes of MnSO4 with different concentrations of CoSO4 and NiSO4.



**Fig. S7.** Charge-discharge curves of (a) the MnO2 and Co-MnO2 cathodes, (b) the MnO2 and Ni-MnO2 cathodes under different areal capacities.



**Fig. S8.** Elemental mapping images of the MnO2 cathode. (a) STEM image, (b) Mn, (c) O.



**Fig. S9.** The energy transfer mechanism maps of Mn4+ for all the cathode materials.



**Fig. S10.** FTIR spectra of all cathode materials and carbon felt.



**Fig. S11.** Mn 2p of XPS for (a) the MnO2 cathode and (b) the Co-Ni-MnO2 cathode.



**Fig. S12.** XPS spectra of MnO2 and Co-Ni-MnO2 cathodes: (a) Co 2p, (b) Ni 2p.



**Fig. S13.** XPS spectra of the Co-MnO2 cathode. (a) O 1s, (b) Mn 3s, (c) Co 2p.



**Fig. S14.** XPS spectra of the Ni-MnO2 cathode. (a) O 1s, (b) Mn 3s, (c) Ni 2p.



**Fig. S15.** EIS of the MnO2/Zn and Co-Ni-MnO2/Zn cells. The inset shows an equivalent circuit.



**Fig. S16.** Charge current response vs. time of the MnO2/Zn and Co-Ni-MnO2/Zn batteries during chronoamperometry charge at 2.2 V to an areal capacity of 10 mAh cm-2.

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