Supporting Information

A high voltage aqueous zinc-manganese battery using hybrid alkaline-mild electrolyte

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Experimental section

Preparation of the Na\(^+\)-form Nafion membranes: The Nafion membrane (DuPont American) was immersed in a beaker containing 3 wt% H\(_2\)O\(_2\) aqueous solution, and the beaker was kept at 60 °C for 1 h. Then, it was rinsed with deionized water several times to remove the remaining H\(_2\)O\(_2\). After, the Nafion membrane was immersed in 0.5 M H\(_2\)SO\(_4\) aqueous solution beaker, the beaker was kept at 60 °C for 1 h, and washed with deionized water to pH close to 7 to remove the remaining H\(_2\)SO\(_4\). Next, 1 M NaCl aqueous solution was prepared (pH is adjusted to 1 by using HCl) in the beaker, Na\(^+\)-form Nafion membranes was immersed in the solution, and the solution was kept for 3 h at 60 °C in order to convert H\(^+\) into Na\(^+\) in the Nafion membrane. Finally, the Nafion membrane was washed with deionized water and stored in deionized water for future use.

Preparation of manganese dioxide: In accordance with the method in the literature\(^1\), 0.003 M MnSO\(_4\)·H\(_2\)O and 2 ml 0.5 M H\(_2\)SO\(_4\) were placed in the beaker and 90 ml of deionized water was added, and the beaker was stirred on a magnetic blender until a clarification solution was obtained. Then, 20 ml 0.1 M KMnO\(_4\) aqueous solution was slowly added to the solution. At room temperature, the mixture was stirred for 2 h. The solution was then transferred to an autoclave lined with Teflon and further placed in an oven at 120 °C for 12 h. After cooling, the mixture was washed three times with deionized water and filtrated to collect the resulting material. Finally, the substance was placed in a vacuum oven at room temperature to dry 12 h.

Cell assembly: The working electrode was fabricated by casting the slurries of prepared MnO\(_2\), acetylene black and polytetrafluoroethy (PTFE) in the weight ratio of 70:20:10, and then dried under infrared baking lamp for 1 h. After drying, the carbon felt was acted as the current collector.

The AZMB was made up of two glass cylinders with a Na\(^+\)-form Nafion membrane in between. The electrolyte at the positive electrode side was 2 M ZnSO\(_4\) + 0.1 M MnSO\(_4\), and the electrolyte at the negative electrode side contained 1 M NaOH + 0.01 M Zn(AC)\(_2\). The fabricated AZMB had a configuration of Zn metal/1 M NaOH + 0.01 M Zn(AC)\(_2\)/ Na\(^+\)-form Nafion membrane/ 2 M ZnSO\(_4\) + 0.1 M MnSO\(_4\)/ MnO\(_2\). A paraffin film was used to seal the zinc plate part in contact with
the interface between electrolyte and air, to avoid the serious corrosion of zinc plate at the interface.

The Zn//MnO$_2$ battery with mild electrolyte was assembled in a two-electrode cell with MnO$_2$ as the positive electrode and Zn as negative electrode, whose electrolyte was 2 M ZnSO$_4$ +0.1 M MnSO$_4$.

The Zn//carbon black cells were assembled like ZMBH. However, unlike ZMBH, these cells were use 2 M ZnSO$_4$ solution with or without MnSO$_4$ as electrolyte at the side of the positive electrode.

**Characterization:** The crystalline characteristic of as-prepared samples was identified by X-ray diffractometer (XRD, D/MAX-IIA, Rigaku) with Cu Kα radiation ($\lambda = 0.15406$ nm) at a scanning angle (2θ) range of 10° to 90°. Morphology and microstructure observation for samples were measured by scanning electron microscopy (SEM, Hitachi Regulus 8100) and transmission electron microscope (TEM, JEM-F200). The surface element analysis of the composite materials was conducted by X-ray photoelectron spectroscopy (XPS, K-Alpha 1063).

**Electrochemistry measurements:** The galvanostatic charge-discharge was performed with a battery tester (LAND) at room temperature, and the cyclic voltammetry (CV) was measured on an electrochemical workstation (CHI 660E). All electrochemical tests are performed under environmental conditions. All values of a specific capacity are based on the quality of the cathode material, excluding the quality of anode and current collector, if there are no other regulations.
Fig. S1 TEM image of the as-prepared MnO$_2$. 
Fig. S2 CV curve of the Zn//MnO$_2$ battery with mild electrolyte at 0.1 mV s$^{-1}$.

Fig. S3 Charge/discharge curves in the initial two cycles: a) ZMBH; b) the Zn//MnO$_2$ battery with mild electrolyte.
Fig. S4 Cycle performance of the Zn//Carbon cell with different electrolytes at the positive electrode side at 300 mA g⁻¹: (a) 2 M ZnSO₄ and 0.1 M MnSO₄ and (b) 2M ZnSO₄; c) Comparison of discharge specific capacity in different positive electrolytes; d) Charge/discharge curves of the Zn//Carbon cell with 2 M ZnSO₄ and 0.1 M MnSO₄.

Fig. S5 SEM image of MnO₂: a) Fresh electrode; b) electrode after charging.
Fig. S6 XRD patterns of MnO₂ electrodes after charge process in different cycles.

Fig. S7 XPS of MnO₂ electrodes during first charge/discharge process at 100 mA g⁻¹ (a) Mn 2p; (b) Na 1s.

References: